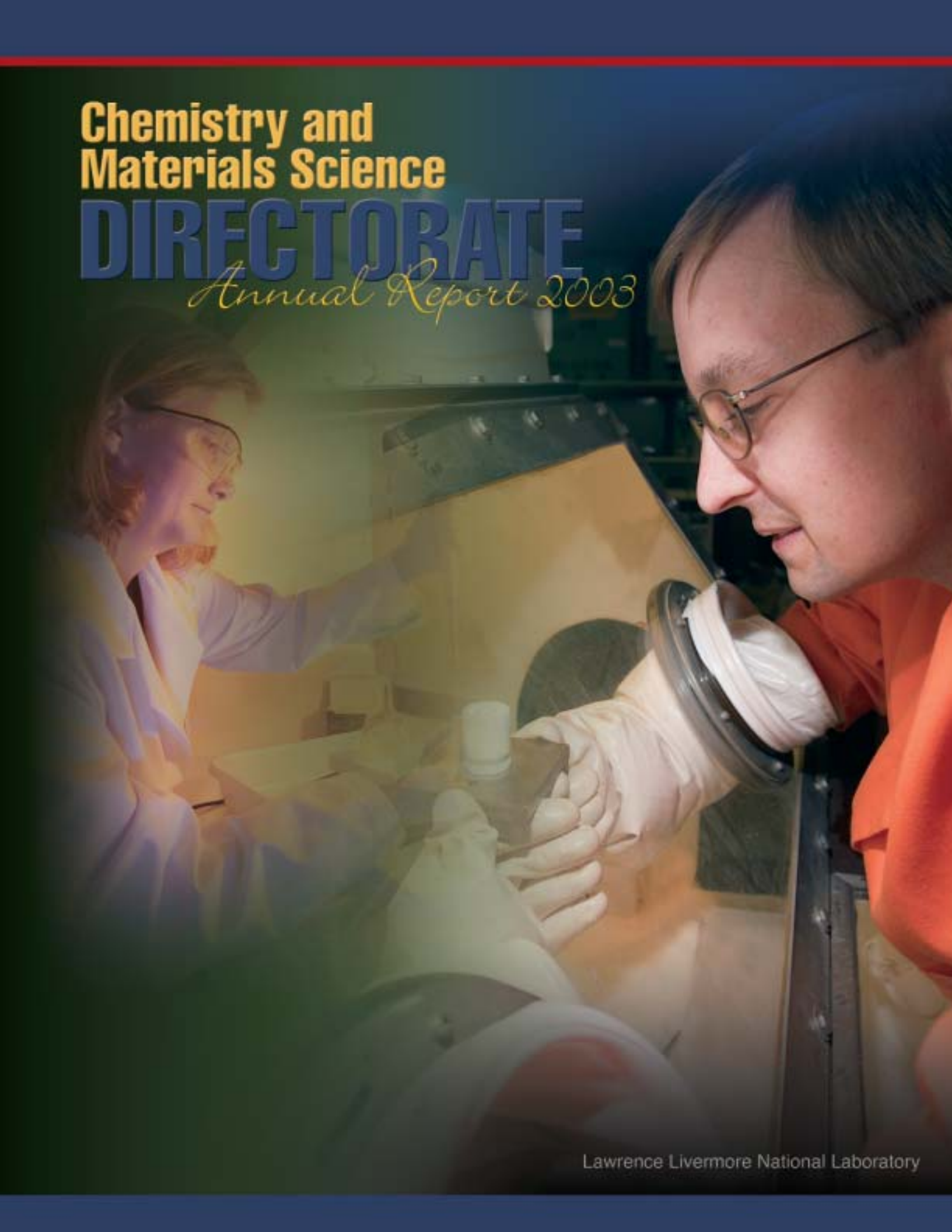


Chemistry and Materials Science

DIRECTORATE

Annual Report 2003



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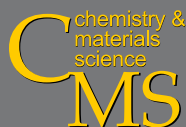
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A message from Tomás Díaz de la Rubia



Evolving challenges and solid accomplishments define the year 2003 for us. Our scientific breakthroughs validate our strategic directions and reaffirm our critical role in fulfilling the Laboratory's missions. Our growth continues in new research projects and significant new programmatic support.

Our mission is clear: to enable the Laboratory to accomplish its primary mission through excellence in the chemical and materials sciences. The directorate's common theme and determination has remained constant:

Deliver on our commitments, while anticipating and capitalizing on opportunities through innovation in science and technology.

In this, the 2003 Annual Report, we describe how our science is built around a strategic plan with four organizing themes, each with key scientific accomplishments by our staff and collaborators. Our strategic plan is synergistic with the Laboratory's Long-Range Science and Technology Plan, which identifies six areas of institutional research and development strategy (see facing page).

This 2003 CMS Annual Report is organized into two major sections: research themes and dynamic teams. The research-theme section addresses challenges, achievements, and new frontiers



within each of the four research themes. The dynamic-teams section illustrates the directorate's organizational structure of divisions, centers, and institutes that supports a team environment across disciplinary and institutional boundaries.

The research presented gives substantive examples of how we are proceeding in each of these four theme areas and how they are aligned with the institutional strategy. Our organizational structure offers an environment of collaborative problem-solving opportunities, an environment that attracts and retains the best and the brightest from across the Laboratory and around the world.

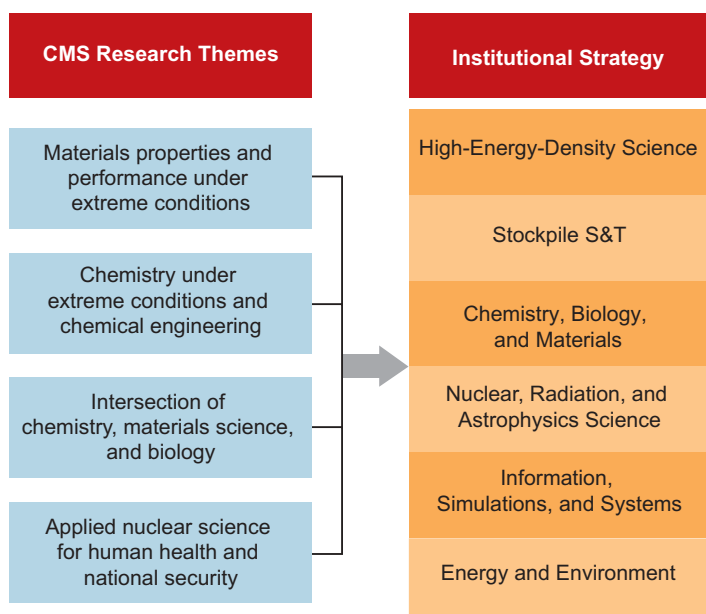
Materials Properties and Performance under Extreme Conditions

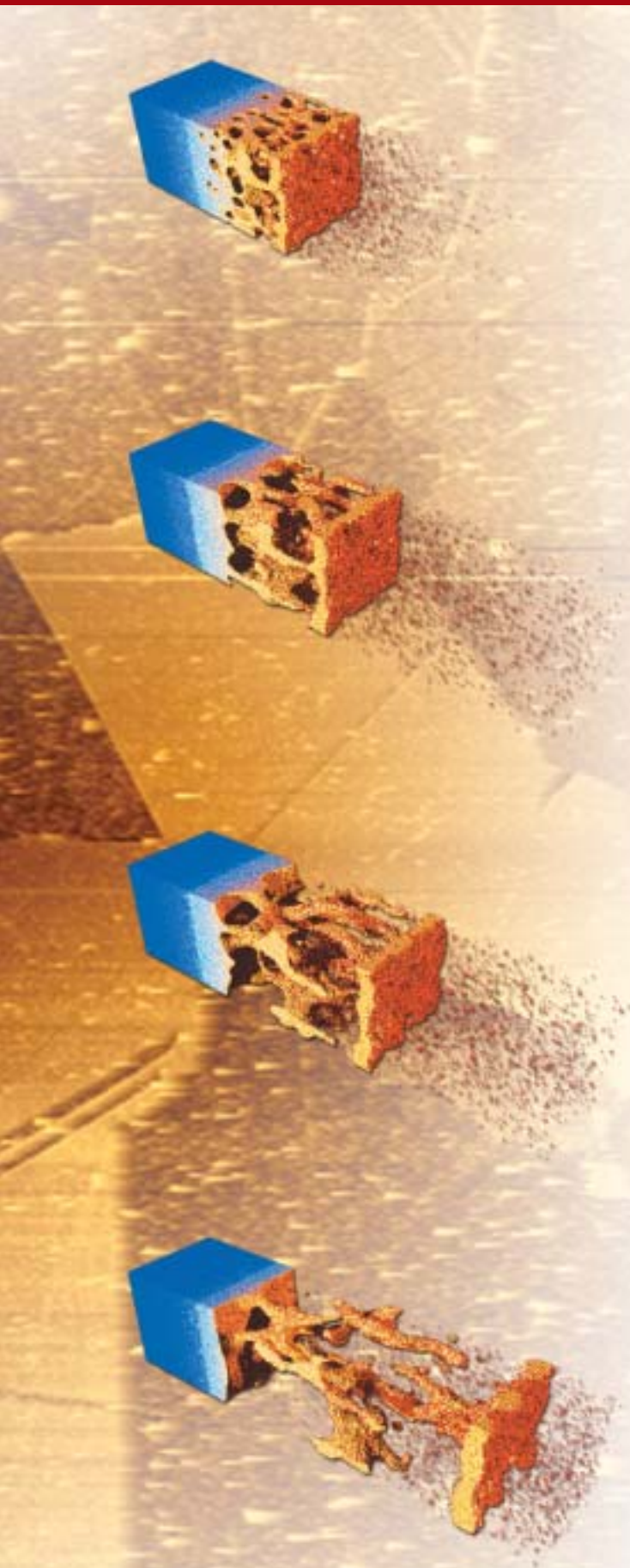
The properties of materials—in particular those of metals and actinides—offer critical insight into our understanding of their performance and, more importantly, their failure mechanisms. The five articles highlighted under this research theme showcase fundamental investigations of matter under extreme conditions, with an emphasis on materials of interest to Laboratory programs and mission needs.

Two studies in materials modeling, dislocation dynamics in metals and modeling laser ablation of metals, exemplify our multiscale modeling methodologies and provide clear examples of how computational materials science can be used—in conjunction with experiments—to understand the dynamical response of metals under extreme conditions. Another landmark event is the first complete measurements of plutonium phonon dispersion, which is also the first experimental validation of emerging new theoretical calculations for correlated electron systems.

Chemistry under Extreme Conditions and Chemical Engineering in Support of National-Security Programs

Taking advantage of the immense computing resources at Livermore, our scientists have enormous opportunities not only to study the extreme phenomena of chemical detonation but also to decipher the chemistry of life. For the first time, we





have successfully simulated the complex water–vapor interface with accuracy and detail never seen before. Our ability to approach multiscale modeling of extreme chemistry is best illustrated in our latest modeling of shock waves. This work adds to our fundamental understanding of chemical reactions of materials through models of molecular response to extreme conditions of temperature and pressure.

A new generation of optical materials has contributed to the many successes in high-power laser science. Specifically, our high-performance diffraction gratings—with their high efficiency and uniformity—are enabling the scientists to study matter under extreme conditions.

Science in Support of National Objectives at the Intersection of Chemistry, Materials Science, and Biology

We actively collaborate with the broader scientific community to provide the capability needed for the development of new technologies and tools for combating terrorism and for fundamental biology and human-health applications. A testament to this capability is our recent advances in single-molecule science, particularly in the studies of protein-folding kinetics as well as conjugated polymers.

Our technological advances are also described in our effort to examine pathogen surface structures with high-resolution atomic force microscopy. We are applying this and many other technologies in our collaborations with national and international agencies. For example, because of its unique capabilities in chemical analysis and forensic characterization of unknown samples, Livermore's Forensic Science Center has been certified to support the Chemical Weapon Convention in the identification of chemical warfare agents.

By combining these technologies, we hope to synthesize and predict molecular interactions in complex environments to support Livermore's mission in sensing and to sustain a strong life-science effort.

Applied Nuclear Science for Human Health and National Security

Undoubtedly, the most far-reaching scientific accomplishment in this area was the synthesis of two new elements, 113 and 115, extending the periodic table further into the region called the “island of stability.” This collaborative work with Russian scientists in Dubna underscores both the value of basic research and the benefit of unfettered international scientific collaboration.

Nuclear scientists in CMS are also breaking new ground in the characterization of elements and isotopes. With tools such as the high-spatial-resolution NanoSIMS and the high-sensitivity

gamma-ray imagers, our scientists are advancing the detection technology for many national-security as well as human-health applications.

Dynamic Teams

CMS is organized to represent the culture of our directorate—discovery-class science and a dynamic organizational structure. We have five crosscutting scientific centers that are staffed by personnel from our three divisions.

The three divisions in CMS are responsible for the line management and leadership of the scientific, technical, and administrative staff. Each division maintains a close relationship with Laboratory programs, working with directorate and program leaders to ensure an effective response to programmatic needs. The divisions conduct scientific and technical research in support of one or more of the four research themes.

The centers provide specific research environments to support needs in biosecurity and nanobiotechnology research; forensic science for chemical, nuclear, biological, and high-explosives counterterrorism; nanoscale synthesis and characterization of novel and alternative materials for Laboratory program applications; applied nuclear science and nuclear radiochemistry; and research and development of high explosives, pyrotechnics, and propellants.

Awards and Recognition

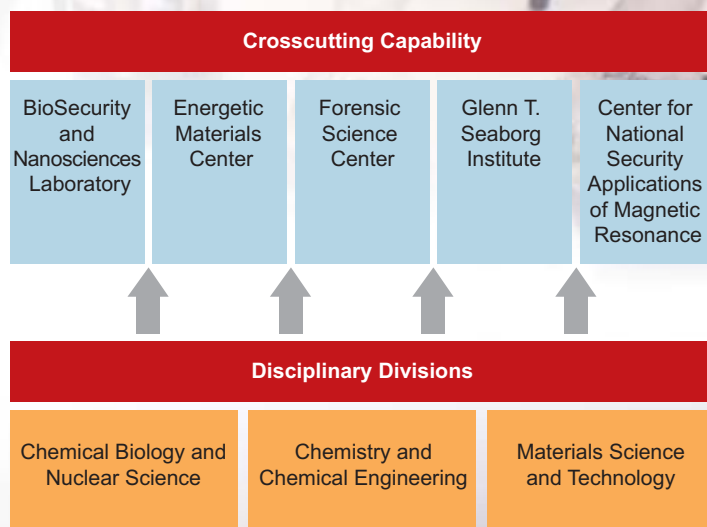
The staff that makes the science happen continues to receive recognition for their accomplishments from their peers through awards, honors, and fellowships from respected scientific societies. The awards and recognition section of this report highlights the many achievements in CMS during 2003.

We have good reasons to be optimistic as 2004 unfolds and the Laboratory sees increasing responsibilities in new national-security programs. CMS has an unambiguous role to play both as a partner and as a technology leader for these responsibilities. More confident and committed than ever, we look forward to expanding frontiers of science and continuing our legacy of partnership with the Laboratory and the worldwide scientific community, as we apply science and technology to the important challenges of our time.

Sincerely,

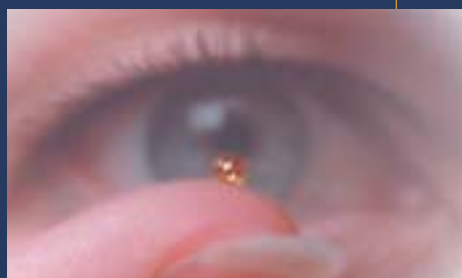


Tomás Díaz de la Rubia
Associate Director, Chemistry and Materials Science
Lawrence Livermore National Laboratory

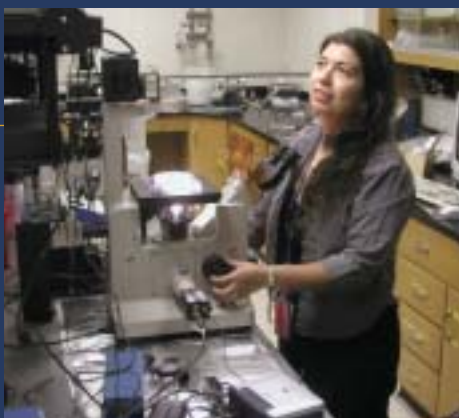


Chemistry and Materials Science

Directorate



Research Themes



Materials properties and performance...

Chemistry under extreme conditions...

Science in support of national objectives...

Applied nuclear science...



Dislocation Dynamics in Metals

Plastic deformation of crystals, including most metals and semiconductors, is known to result from the motion of many dislocation lines. A strong shock, for example, induces numerous dislocations within a metal's crystalline lattice, which changes the metal's mechanical properties such as its strength, ductility, and resistance to cracking. Prediction of the strength of a single crystal against plastic deformation is possible by modeling the dynamics of dislocation lines under external stress and interactions with other dislocations. However, the major difficulty in modeling the condition is that dislocation activities

across a wide range of length and time scales need to be accounted for in order to describe crystal plasticity accurately. While single dislocations and reactions between a few of them are controlled by mechanisms at the atomistic scale, dislocations also produce long-range elastic fields and spontaneously organize themselves into highly complex microstructures over distances of micrometers or longer during plastic deformation.

Currently, we model dislocation dynamics at the atomistic, microscopic, and continuum levels, with an emphasis on connecting these different length scales. The massively parallel computing

resources at Livermore provide unique opportunities to connect them effectively. The multidisciplinary nature of many important dislocation dynamics problems ensures that we work in collaboration with other experts at the Laboratory.

Relevance to CMS Research Themes

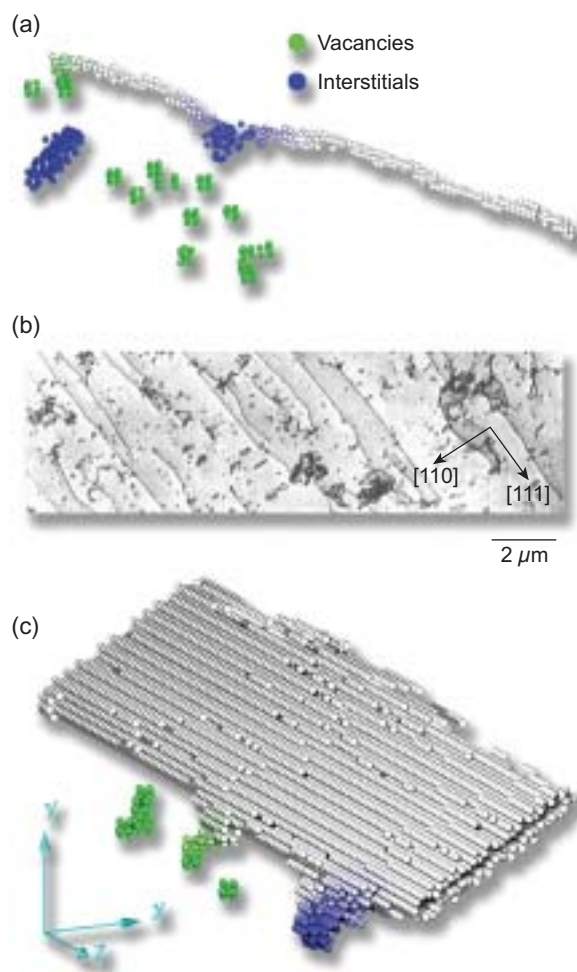
The Laboratory's defense-related mission requires an understanding of how metals respond to the sudden shock waves and subsequent high-strain-rate deformations. To assess materials properties and performance under extreme deformation conditions, we need to understand the fundamental origin of deformation and strength, because direct measurements of materials properties under extreme conditions are difficult. For metals, this task amounts to quantitatively understanding how the resistance against plastic deformation arises from the collective dynamics of lattice dislocations. Such understanding can then be built into numerical models that will provide accurate predictions of materials response under extreme conditions.

Our computer simulations play an important role in this endeavor, particularly when they are linked to experimental results. The greatest value to stockpile science and technology is realized when computational models accurately predict dynamic material failure and identify the conditions where the comparison between experimental measurements and theoretical predictions would yield maximum insight and fundamental understanding of complex dynamical processes.

Major Accomplishments in 2003

Atomistic simulations have shown that dislocations can respond to extreme conditions of high stress (or high strain rate) in unexpected ways. We studied the motion of a screw dislocation line in pure, body-centered cubic (bcc) iron using molecular dynamics. At low stress, the dislocation moves forward smoothly, but at higher stress, the dislocation stress

Figure 1. (a) A screw dislocation in body-centered cubic iron self-roughens and leaves point defects behind while moving under high stress in a molecular dynamics simulation. (b) Similar microstructure has been previously found in body-centered cubic metals. (c) At even higher stress, the same dislocation stops moving and nucleates a twinning plate. The moving dislocation produces equal numbers of vacancies (green points) and interstitials (blue points), but the vacancies seem to be scattered while the interstitials come in large clusters.





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spontaneously roughens and produces point defects (Figure 1). Similar microstructures have been observed frequently in bcc metals without a satisfactory explanation. Previous experimental studies had suggested that impurities or additional dislocations were responsible for this behavior, but since these were not present in our simulations, our results strongly suggest that this behavior is intrinsic to a moving dislocation. In other molecular dynamics simulations of face-centered cubic aluminum, we uncovered a new, anomalous mechanism of dislocation multiplication at high stresses.

Under applied stress, individual dislocations also interact with each other. This critical step has been the bottleneck for a quantitative understanding of plasticity, because past computational models could not follow the dynamics of large enough numbers of dislocations for a long enough time. In response, we have developed a new massively parallel dislocation dynamics code, ParaDiS, to study problems with very complex dislocation microstructures (Figure 2). For example, previous models were able to simulate the relationship between tensile stress and tensile strain only to about 0.1 percent strain, where the number of dislocations begins to grow rapidly. Using ParaDiS, we have been able to extend the analysis to 0.3 percent and much lower hardening rate to 1.5 percent strain, suggesting a new recovery mechanism. This new capability enables us to address the two key features, hardening and recovery, of the long-standing problem of plasticity.

Future Goals

We anticipate that by 2006, deformation simulations with 10 percent strain would be standard calculations, using next-generation supercomputers such as BlueGene/L with its more than 100,000 processors. ParaDiS has been selected as one of BlueGene/L's early applications. Connecting atomistic models

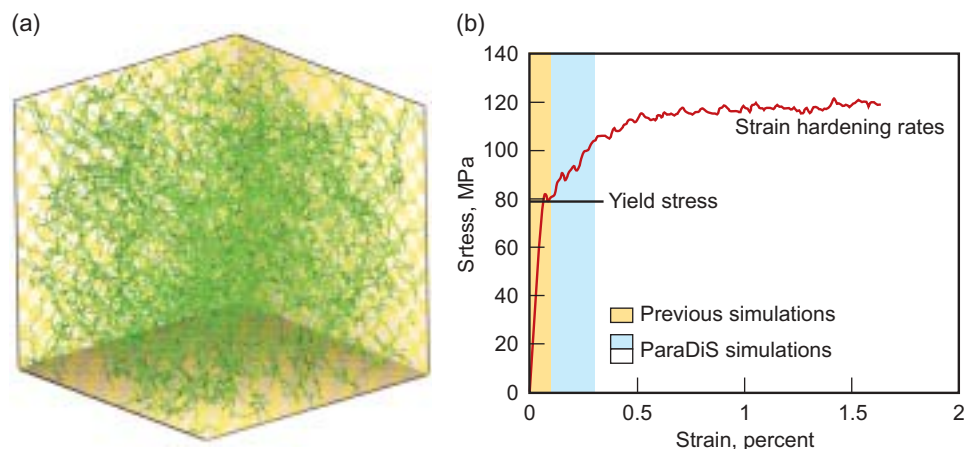


Figure 2. (a) A massively parallel dislocation dynamics simulation produced by the ParaDiS code shows detailed dislocation microstructure. Simulation cell size is 10 μm . (b) Stress-strain relationship predicted by this simulation shows yield, hardening, and recovery phenomena.

and ParaDiS is an important target, which will require formulation of numerically efficient code modules to incorporate the behaviors we are discovering from atomistic simulations into large-scale dislocation line simulations. At the same time, ParaDiS simulations will provide new insights into important features such as spontaneous formation of new microstructures and their temporal evolution. Such insights will be useful in constructing new continuum models of crystal plasticity, which promise efficient and predictive tools for engineering applications.

Related Publications

Marian, J.; Cai, W.; Bulatov, V.V. Dynamic Transitions from Smooth to Rough to Twinning in Dislocation Motion, *Nature Materials* **2004**, 3, 158.

de Koning, M.; Cai, W.; Bulatov, V.V. A Mechanism for Anomalous Dislocation Multiplication in FCC Metals, *Physical Review Letters* **2003**, 91, 022503.

Cai, W. et al. Massively Parallel Dislocation Dynamics Simulations, *IUTAM Symposium on Mesoscopic Dynamics of Fracture Process and Materials Strength*, Osaka, Japan, July 7–11, **2003**, Kluwer Academic Publishers, in press.

New Frontiers

Many novel materials have heterogeneous microstructures. The mechanical properties of these materials are strongly influenced by the mechanics of their internal interfaces, the most common of which is a grain boundary. Interactions between grain boundaries and other lattice defects are responsible for many mechanical behaviors of polycrystals. A grain boundary can block the dislocation motion in one grain and can emit new dislocations into the other grains.

Dislocations absorbed by a grain boundary will assist the sliding of the interface. Atomistic simulations have helped us identify the mechanisms of these interesting interactions between dislocations and grain boundaries. The challenge before us is to develop larger-scale simulations of these complex systems and minimize simulation artifacts. Continued advances in computer capabilities and modeling techniques will enable us to realize our goals in our research.

Metal and Metal-Oxide Interfaces in Corrosive Environments

All metals and metal alloys eventually corrode, some faster than others. The most familiar corrosion process is rusting or oxidation. Corrosion problems affect two major Livermore programs. The first program area involves metal components in the U.S. nuclear stockpile that need to remain functional for many years longer than their intended lifetime. The second area relates to the nuclear waste repository storage containers at Yucca Mountain, which are intended to remain intact for 10,000 years. It is therefore very important to understand the fundamentals of corrosion in order to develop extremely corrosion-resistant materials.

Electrochemical phenomena that occur at surfaces—such as corrosion, dissolution or oxidation—are known to depend on the crystallographic orientation of the underlying material. Most surface science approaches to corrosion have focused on well-oriented single crystals of pure metals and have demonstrated different corrosion rates for the principal orientations of both cubic and non-cubic crystals. For simple cases, this anisotropy results from the different binding energy of surface atoms in each orientation. Close-packed planes have higher binding energy due to their higher atomic coordination; therefore, the dissolution is slower.

To advance understanding of metal and metal alloy corrosion, our work has produced a fast method to obtain a complete survey of all grain orientations simultaneously, allowing a correlation between metal structure and anisotropic surface processes.

Relevance to CMS Research Themes

Developing a fundamental understanding of the corrosion process has dramatic technological and economic consequences in industrial societies. Gathering sufficient knowledge to be able to confidently predict consequences over centuries is very challenging, which is why this work is identified with the CMS theme area of extreme materials. The areas of energy and environment as well as stockpile science and technologies in Livermore's long-range plan are affected by this work.

Major Accomplishments in 2003

We combined electron back-scattered diffraction (EBSD) imaging with atomic force microscopy (AFM) to correlate the crystallographic orientation of grains at the surface of the alloy with the rate of corrosion at the nanometer level. We etched a corrosion-resistant nickel, chromium, and iron alloy called Inconel with hydrochloric (HCl) acid to accelerate corrosion. Comparisons between the EBSD image of the original sample and AFM images of the same sample after it was etched demonstrated clearly that the crystal grains corrode at different rates (Figure 1). Pure dissolution suggests that the etching rate should inversely correlate with atomic packing density of the surface, which is greatest for the (111) orientation and smallest for the (101) orientation. Our corrosion rates do not follow this rule, suggesting that oxidation and diffusion play a role. Also, the surface morphology of these regions,

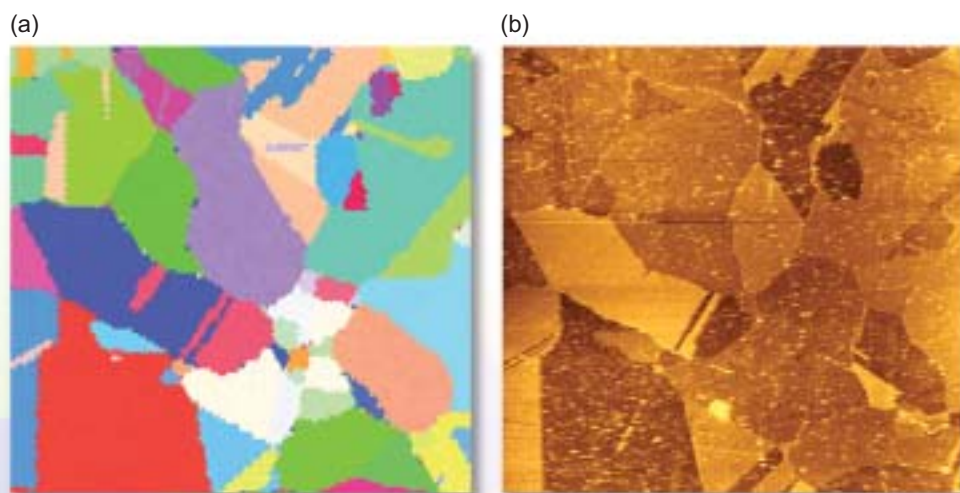


Figure 1. (a) A 100-by-100- μm section of an electron back-scattered diffraction image of an Inconel surface. The colors represent different grain orientations [blue=(111), green=(101), and red=(001)]. (b) An atomic force microscopy image of the same area after etching slightly in dilute HCl. The degree of etching (corrosion) is proportional to the darkness of the etched region. The grains nearest the (111) direction etch the least, while those nearest the (001) direction etch the most.



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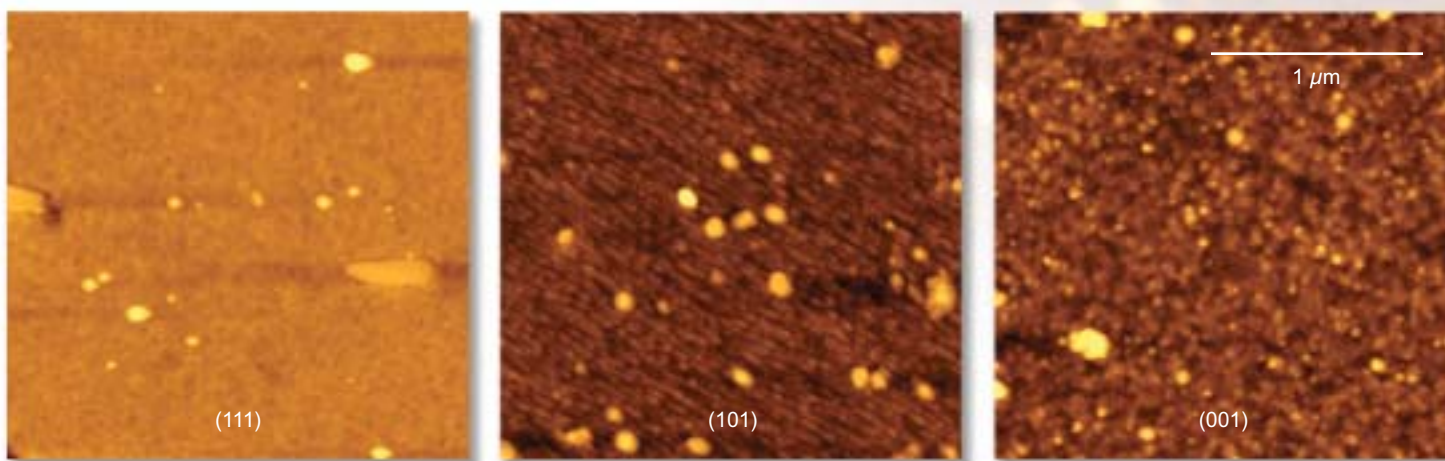


Figure 2. Atomic force microscopy images of corroded surfaces on the three crystallographic orientations after HCl treatment show different features. The (111)-oriented grains corrode the least. The oxide appears compact and smooth. The (101)-oriented grains have an intermediate corrosion rate. The oxide has a striped morphology; the stripes align with the (111) family of planes. The (001)-oriented grains corrode the most. The oxide has an open, porous morphology. Each figure is approximately $4 \mu\text{m}^2$.

obtained by AFM at greater resolution (Figure 2), showed different features for each of the grain orientations as well.

These results are consistent with the existence of an oxide layer on the surface of the Inconel. Our results provide a valuable step to understanding the factors involved in corrosion of metals. We also found that the correlated use of EBSD and AFM offers a powerful method for rapid study of anisotropic surface properties.

Future Goals

We plan to study the dynamics of dissolution and re-passivation by imaging these processes using in situ AFM under electrochemical control. In the example shown above, the faces etch at different rates, while in other systems, etching occurs preferentially at grain boundaries. In these systems, we can correlate the type of grain boundary with dissolution dynamics. Other groups use metallurgical processing steps to

manipulate the grain orientation and types of grain boundaries at a surface. With insights from the above work, it may be possible to connect these relatively inexpensive processing steps with improved corrosion performance. The in situ studies are also ideally suited to understand the way in which corrosion inhibitors interact with the surface and limit dissolution.

Related Publications

Schuh, C.A.; Anderson, K.; Orme, C. Rapid Assessment of Anisotropic Surface Processes: Experiments on the Corrosion of Inconel 600. *Surface Science* **2003**, *544*, 183–192.

Bearinger, J.P.; Orme, C.A.; Gilbert, J.L. Effect of Hydrogen Peroxide on Titanium Surfaces: In Situ Imaging and Step-Polarization Impedance Spectroscopy of Commercially Pure Titanium and Titanium, 6-Aluminum, 4-Vanadium. *Journal of Biomaterial Research* **2003**, *67A*, 702–712.

New Frontiers

The long-term goal of this project is to develop the techniques for in situ, microscopic observation of electrochemical events in fluid environments. Scanning probe microscopy—in combination with optical spectroscopies such as Raman, ellipsometry, and polarized reflectance spectroscopy—will be used to determine the mechanisms of dissolution, deposition, and adsorption in aqueous environments. Ultimately, we expect that understanding the mechanisms of corrosion will lead to new materials and processing steps that reduce corrosion rates and allow materials to be designed for desired lifetimes. In addition, our findings will allow us to predict lifetimes with confidence. More generally, knowledge from in situ observation of electrochemical events can be applied towards diverse applications, from the electrodeposition of metal for target fabrication to the adsorption of biological molecules in electrochemical sensors.

Modeling Laser Ablation of Metals at the Atomic Scale

Laser ablation is the process of irradiating the surface of an object with a beam of sufficient energy to eject some of the material, allowing the sculpting of the surface with a wide variety of complex patterns. However, a limitation of this method has been its tendency to leave a rough surface, with perturbations on a micrometer length scale that degrade the quality of the pattern, as illustrated in Figure 1. In order to develop methods to ameliorate the roughening, we have simulated short-pulse ablation, using large-scale atomistic models and a continuum approach.

Multiscale modeling is required to treat the wide range of length and time scales involved. In this application, the one-dimensional HYADES code is used to treat the first picoseconds of the process, including the interaction of the radiation with the electrons and the transfer of kinetic energy from the electrons to the atomic nuclei. Subsequent three-dimensional motion of the atoms is modeled using the molecular dynamics code, MDCASK.

Relevance to CMS Research Themes

Theoretical and modeling methods are useful in studying materials processing techniques that use short-pulse lasers.

These techniques are performed in a highly non-equilibrium and extreme environment. Developing computational capabilities provides accurate predictions of materials response. The models complement experiments because they provide information about extremely short time events that are difficult for high-resolution microscopy to capture. The results will advance our ability to produce precise, engineered target systems for high-energy-density experiments. The methods developed will also prove valuable in understanding materials performance in many stockpile stewardship efforts.

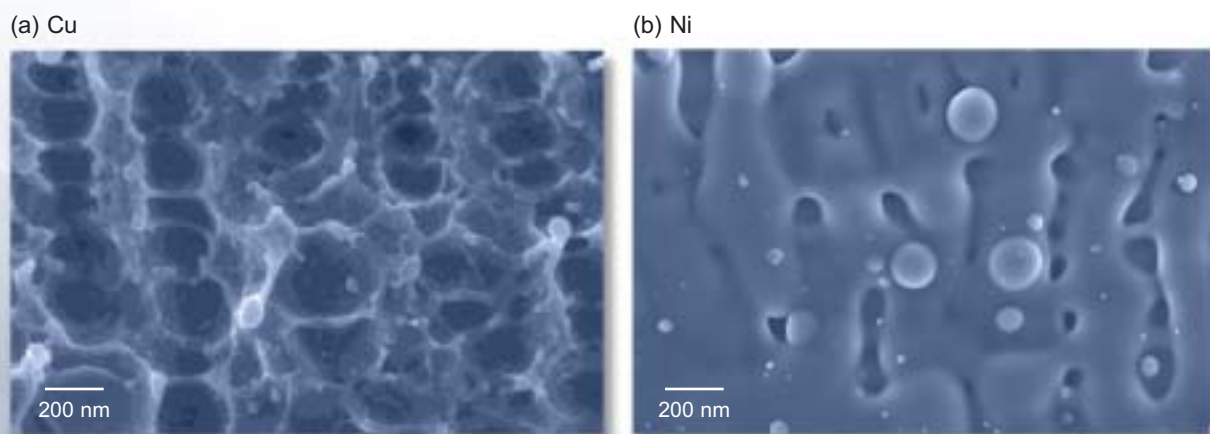
Major Accomplishments in 2003

We modified MDCASK to incorporate the data from HYADES on the interaction of the radiation with the materials and on heat conduction. Using Livermore's Intel Linux cluster, we simulated systems with up to 30 million atoms. The large system size allowed us to study void nucleation and surface evolution on unprecedented length and time scales. We also investigated the ejection of liquid droplets, a phenomenon observed in experiments. Three distinct regimes were exhibited in the simulations: (1) low pulse-energy-

densities where only a minute ablation flux results from the evaporation of atoms from the hot metal surface; (2) an intermediate regime, where void nucleation and growth, or spallation, causes the ejection of a liquid layer several nanometers thick; and (3) high pulse-energies that eject liquid droplets with a wide range of sizes. Figure 2 shows an example of a simulation of copper ablation, illustrating the intermediate-energy-density regime. The liquid layer of the simulation explains in detail interference fringes previously observed by femtosecond pulse-probe experiments.

We are using MDCASK to investigate a procedure to lay down a uniform, thin film on a non-wetting substrate. For this technique, the pulse-energy-density would be set to ablate the liquid film. The advantage of the sudden impact of an intact film with the substrate is that it would inhibit the formation of three-dimensional islands. The method may, for example, allow the deposition of thin films of refractory metals on low-temperature substrates for use in the National Ignition Facility (NIF) applications. Also, based on the understanding developed from the simulations, we have identified a

Figure 1. High-resolution scanning electron microscope of (a) copper and (b) nickel surfaces after a single 800-nanometer, 1-joule-per-centimeter-squared pulse. Note the smoother surface left behind in the case of nickel.





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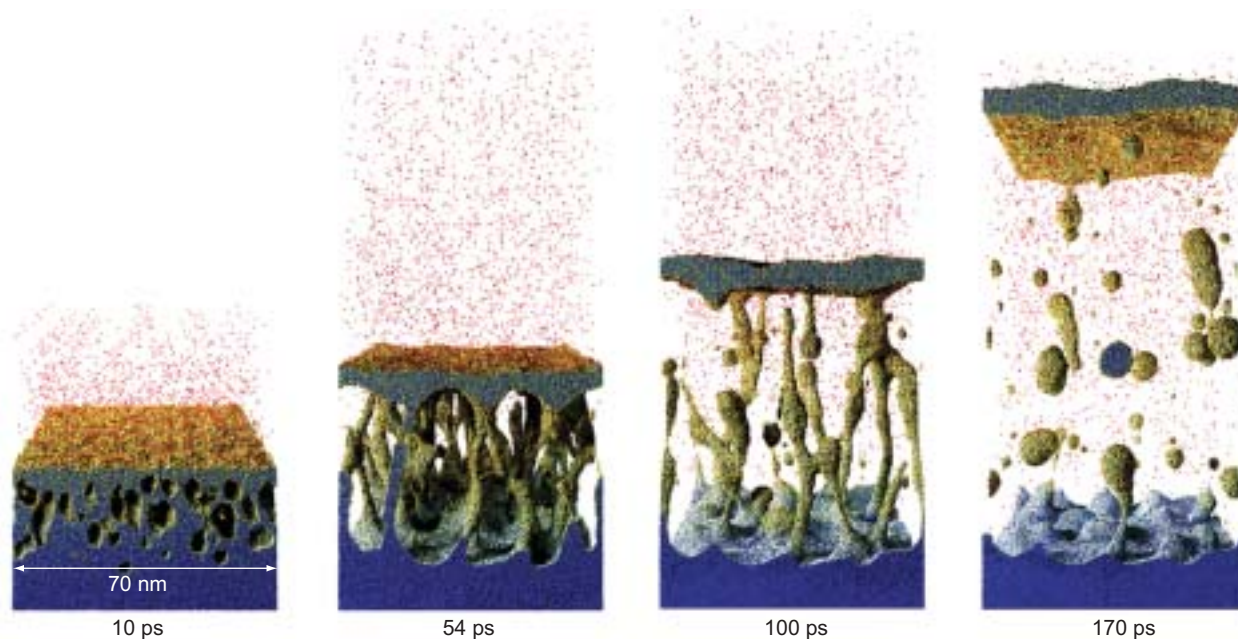


Figure 2. Snapshots from molecular dynamics simulations of ablation, using a 100-femtosecond, 800-nanometer laser pulse on the upper surface of a copper crystal. The cross-section of the copper crystal is a square, 64 nanometers on an edge. Note that atoms shown in the figure are either located at an interface with the vapor, or visible because they are at the boundary of the computational cell. In the latter case, they are mostly in the bulk liquid or crystal, with neighbors on all sides because of the periodic boundary conditions. These atoms tend to have lower potential energies than those at the liquid/vapor interface and, therefore, have a different color than the atoms at the interfaces.

technique to reduce surface roughening during laser machining.

Future Goals

Using accurate models derived from the theory of plasma dynamics, we plan to improve the molecular dynamics model to include a new, two-temperature model of an electron sea interacting with the atomic nuclei. This new feature will allow for simulations under conditions where the two systems are far out of equilibrium and will accurately represent the electronic heat conduction in three dimensions for a wide range of temperatures.

We also intend to pursue simulations of the impact of ablated films and droplets with various substrates in order to develop methods to deposit dense refractory films of various metals. We will examine the uniformity of the film, together with its dependence on the materials' properties

(for example, atomic masses and melting temperatures) and the conditions prevailing during ablation. Finally, we hope to develop a continuum model describing the evolution of void, liquid layer, and droplet surfaces during ablation, so that larger surface features can be simulated. The model would allow the extension to longer pulses and ablation effects resulting from non-uniform laser intensity.

Related Publications

Shirk, M.D. et al. Mesoscale Laser Processing Using Excimer and Short-Pulse Ti:Sapphire Lasers. *Proceedings of the International Conference on Applications of Lasers and Electro-Optics*, in press.

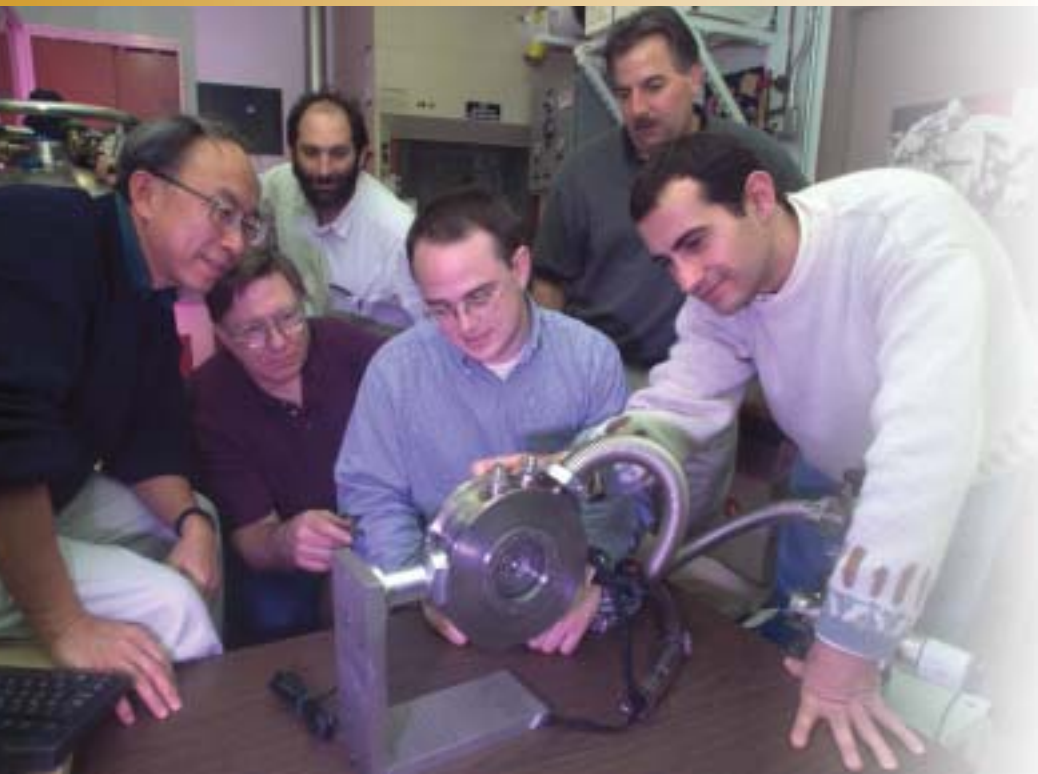
Dalla Torre, J., et al. Microstructure of Thin Tantalum Films Sputtered onto Inclined Substrates: Experiments and Atomistic Simulations, *Journal of Applied Physics* **2003**, 94, 263–271.

New Frontiers

We hope to develop a method to deposit dense smooth films of refractory metals onto a range of substrate materials, including those with relatively low melting points. These could be useful for a number of applications, including the deposition of tantalum diffusion barriers onto semiconductor devices for copper metallization and the fabrication of nanoscale experimental targets.

Improvements in thin-film uniformity by the use of pulsed laser ablation of liquid films could have an impact on a wide range of technologies, including sensors, where very thin films with accurate dimensions are required. The development of laser ablation as an accurate and controlled method to fabricate objects and shape materials such as explosives continues to be pursued by several groups at Livermore.

First Complete Measurements of Plutonium Phonon Dispersions



Phonons are lattice vibrations produced by the movement of atoms in a solid. Their energy variations as a function of crystal momentum along different crystallographic directions, or phonon dispersion curves (PDCs), measure interatomic forces in solids and yield quantum- and atomistic-level information on many physical and structural properties, such as sound velocity, elasticity, heat capacity, and phase stability.

Plutonium has defied phonon measurements since the element's discovery by Glenn Seaborg in 1941. Inelastic neutron scattering, the conventional method used to map phonon dispersions in most solids, cannot be used to map plutonium's PDCs because the method requires large single crystals approximately a few millimeters in size, and it is not possible to grow plutonium crystals this large. Inelastic neutron scattering also would not work for plutonium because of the

high neutron absorption of the commonly occurring ^{239}Pu isotope.

Contributing to the challenge of its study, pure plutonium exhibits six solid-state phase transformations before reaching its liquid state, passing from $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta \rightarrow \delta' \rightarrow \epsilon \rightarrow \text{liquid}$ with large volume expansions and contractions as it is heated from the room-temperature stable α -phase to the molten liquid.

Relevance to CMS Research Themes

Phase-dependent phonon and elastic moduli data are essential enabling ingredients for developing multiphase equations of state and the corresponding strength models. Our PDC measurements impose rigorous constraints on our interatomic-force models that calculate these properties.

Similarly, elastic moduli are fundamental building blocks of multiphase strength models. Even at the macroscopic level, there is generally a linear scaling of

yield strength in metals with the pressure- and temperature-dependent shear modulus. Accurate data are needed to link the multiscale modeling of plasticity and strength from the quantum and atomistic levels to the continuum level.

Major Accomplishments in 2003

Our team performed the first measurements of phonon dispersions in gallium-stabilized delta-plutonium. The phonon data were collected at the European Synchrotron Radiation Facility in Grenoble, France, which has a unique, high-resolution inelastic x-ray scattering (HRIXS) beamline suitable for measuring phonons in plutonium. We directed a high-energy (21 keV), high-brightness x-ray micro-beam onto large-grain polycrystalline specimens prepared from a plutonium–gallium alloy containing approximately 0.6-weight-percent gallium. Single-crystal domains of the fcc delta-plutonium were selected and the scattered x-ray spectra were measured and used to determine the PDCs in the respective longitudinal (L) and transverse (T) modes. The resulting phonon dispersion curves are displayed in Figure 1 as plots of the phonon energy versus the wave vector along the principal crystallographic directions.

From the slopes of the dispersion curves at the Γ point, the elastic moduli can be determined directly. The values indicate a profound elastic anisotropy in delta-plutonium, more than in any other fcc metal known. Data also showed a Kohn-like anomaly, suggesting that the fundamental mechanism for the high-temperature phase transition arises from electron-phonon interactions. The most pronounced feature of the experimental PDCs is that the transverse mode exhibits a substantial softening as it approaches point L. These features may be related to



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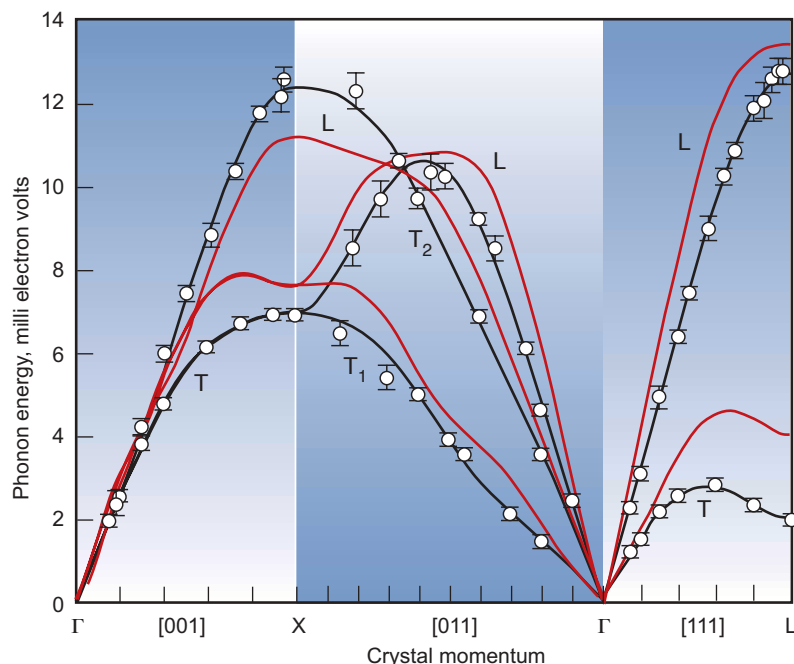


Figure 1. Phonon dispersions along the principal crystallographic directions [001, 011, 111] in a plutonium-gallium alloy. The longitudinal and transverse wave vectors are denoted by L and T, respectively. The experimental data are shown as circles. The black lines are the data's fits to the Born-von Karman model of lattice dynamics. The red lines are theoretically calculated dispersions for pure delta-plutonium based on the recent dynamical mean field theory.

the $\delta \rightarrow \alpha'$ phase transformation at low temperature associated with closely packed (111) planes in the fcc structure.

The resulting dispersion values generally agreed with theoretical calculations based on the dynamical mean field theory (Figure 1). The theory incorporates correlation effects among plutonium's electrons. This landmark experiment opens up new research opportunities in actinide science and provides the first full phonon dispersion curves ever measured for any plutonium-bearing material.

The LLNL team (opposite page) received a 2003 *Director's Science and Technology Award*, the highest honor granted by LLNL for science and technology accomplishments.

Future Goals

Our team will direct its work to studying the effects of combining

different amounts of gallium with plutonium, and in determining how the phonon behavior affects the stability of the various phases of plutonium. Specifically, we will look at the T [111] softening in relation to the $\delta \rightarrow \alpha'$ transformation in plutonium-gallium alloys from its temperature dependence. We will also look at the Kohn anomaly in the T1 [110] branch and its Gruneisen parameters.

Related Publications

Hecker, S.S. Challenges in Plutonium Science, *Los Alamos Science* **2000**, 26, 290.

Wong, J. et al. Phonon Dispersions of fcc δ -Plutonium-Gallium by Inelastic X-Ray Scattering, *Science* **2003**, 301, 1078.

Dai, X. et al. Calculated Phonon Spectra of Plutonium at High Temperatures, *Science* **2003**, 300, 953.

New Frontiers

Our longer-term goal is to further investigate plutonium phonon dispersions as a function of temperature and pressure. While the technical challenges for such experiments are considerable, phonon and elastic-moduli data for correlated-electron materials over wide ranges of thermodynamic conditions are of prime importance in current efforts to develop advanced multiphase equations of state. For instance, the bcc ϵ -Pu phase melts to produce a liquid of higher density. HRIXS measurements of this phase at high temperatures, where it is stable thermodynamically, will shed light on the lattice dynamics and mechanisms associated with the melting process and the $\delta \rightarrow \epsilon$ transition. Likewise, all of the other phases of plutonium are of interest, and a thorough and systematic investigation is needed for a full understanding of the phase diagram and its connection to the complex 5f-electron system.

Unraveling the Phase Diagram of Plutonium

The complex electronic structure of the actinide metals has long been one of the most challenging problems in condensed-matter theory. In particular, the highly unusual electronic structure of plutonium is responsible for one of the most complex phase diagrams of any element in the periodic table. As plutonium is heated from room temperature and pressure to approximately 600 °C, it changes from its ground-state α -phase to β - and γ - and finally δ -phase plutonium. Other important characteristics such as specific volume, crystal structure, and thermal expansion also vary from one phase to another.

Past attempts to explain and simulate the behavior of plutonium, using the techniques of computational materials science and density functional theory (DFT), have been largely unsuccessful,

although occasionally simulations over limited ranges of conditions have reproduced experimental results. Some successes have even been challenged as being coincidental and not due to a correct treatment of the relevant physics.

The enormous importance of plutonium to the U.S. Stockpile Stewardship Program, combined with the theoretical complexity and the scientific interest that plutonium inspires, makes it very desirable to explore the capabilities of highly regarded theoretical techniques, particularly DFT, to describe properties of plutonium.

Relevance to CMS Strategic Themes

Research in the theme area of materials properties and performance under extreme conditions plays a critical role in advancing the stockpile science and technology. A major challenge of Livermore technology is to accurately

predict materials behavior over extraordinarily broad length and time scales. Our ability to do this depends on our fundamental understanding of the organizational principles of matter that are operative in the system. For plutonium, this is an exceptional challenge. Here the focus is on highly correlated electron systems that straddle the boundary of magnetism and superconductivity and where electrons appear to interact so strongly as to yield new materials physics.

Major Accomplishments in 2003

We found that DFT can explain most of the observed phase behavior of plutonium when additional physics features are included in the analysis. We first examined the ground state of alpha-plutonium using a staged application of DFT, beginning with simpler modeling techniques and adding complexity in the physics, one piece at a time. We discovered important consequences when we included the effects of spin-orbit polarization and magnetic interactions caused by the moments of individual plutonium atoms (Figure 1). This is not unexpected when we realize that plutonium is at a boundary that separates superconducting materials from magnetic materials. A rather surprising result of the DFT calculations was that short-range antiferromagnetic ordering of plutonium atoms is a feature of α -Pu that strongly affects its specific volume and its bulk modulus, but that these magnetic effects cancel out over longer spatial scales, making α -Pu appear non-magnetic (Figure 2).

The team systematically applied the same techniques to each of plutonium's phases, including the α , β , γ , δ , δ' , and ϵ phases. We found that if the same factors of spin-orbit polarization and magnetic interactions are properly treated, DFT is capable of producing realistic energies, structures, and many other features of all of these plutonium phases.

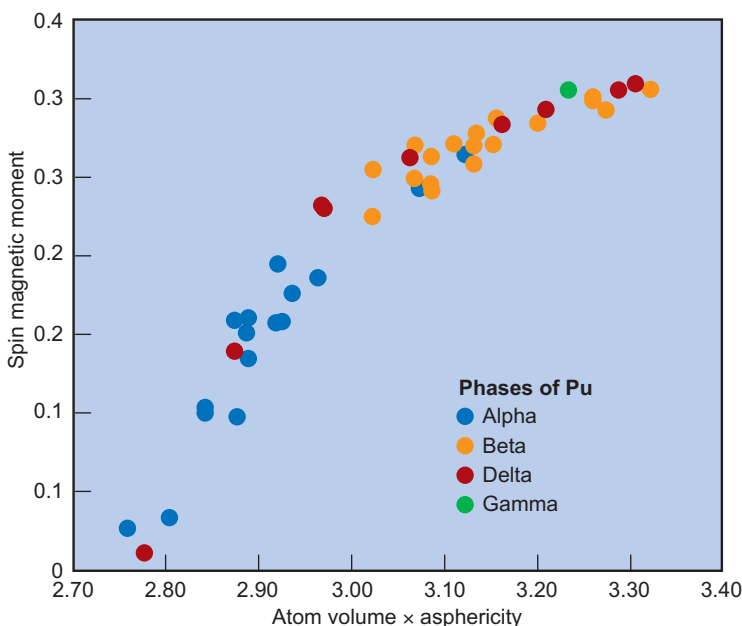


Figure 1. Incorporating spin-orbital polarization allows for accurate prediction of the energy of all the phases of Pu. However, the magnitude of the magnetic moments depends strongly on the lattice structure. This graph shows a universal relationship between local atomic environment and the magnitude of the spin magnetic moments.



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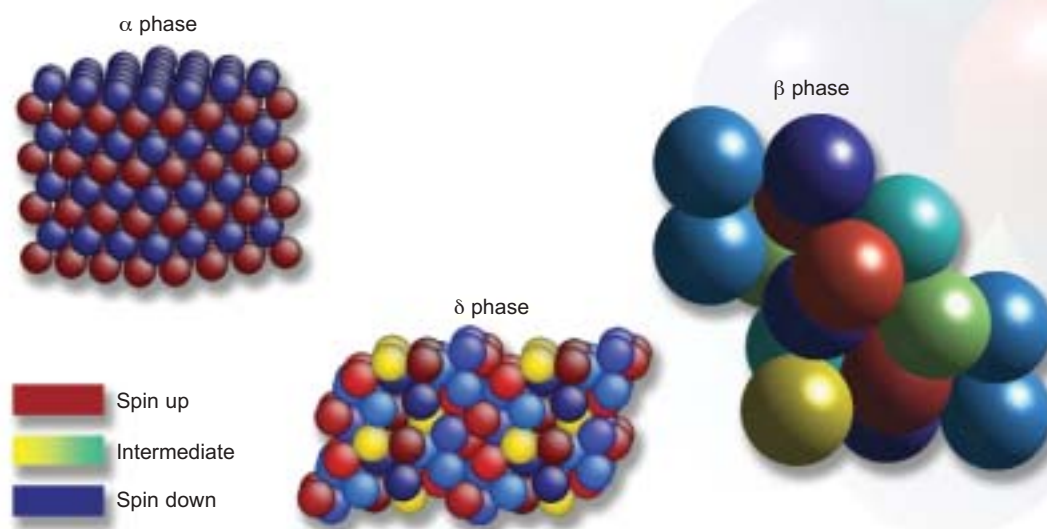


Figure 2. In general, an overall antiferromagnetic spin configuration is preferred for all the different Pu phases. However, for the more distorted structures, many choices are possible. We have discovered that the lowest energy configurations maximize the local antiferromagnetic coupling at each atomic site.

One important consequence of our work is that DFT, a widely used theoretical technique that had been challenged as being inadequate to describe the physics and chemistry of plutonium and other complex systems, has been shown to be entirely adequate for this analysis, but only if the physics of local moments are included in the analysis. Our results mean that for the first time, it is possible to compute many of the important properties of plutonium from first principles, which is an important result for Livermore projects.

We have further utilized this theoretical technique to study the thermodynamics and kinetics of the dilute plutonium–gallium alloys. Their calculations have predicted some properties such as density variations for plutonium and plutonium–gallium alloys that are intriguing and provide an explanation for some of the decades-old puzzles in plutonium physical metallurgy.

Future Goals

Experiments are in progress to test the underlying assumptions on which the predictions of this model are based. The

scaling relations obtained can potentially be applied to fitting empirical potentials, which can then allow for large-scale molecular dynamic studies of plutonium.

The impressive accuracy of DFT shown by these results suggests that perhaps DFT is more powerful than previously believed, and this view should be explored. Based on the experience obtained for plutonium, other condensed-matter systems where DFT has apparently failed, such as metal-oxides, need to be explored. Our goal is to completely study the elasticity of plutonium, as well as the properties of defects in its different phases. The aim is to provide a kinetic model for the martensitic transformation of plutonium from its δ phase to the α -Pu structure.

Related Publication

Sadigh, B.; Söderlind, P.; Wolfer, W.G. Geometry and Electronic Structure of α -Pu: A Theoretical Study, *Physical Review B* **2003**, 68, 241101.

P. Söderlind and B. Sadigh, Density Functional Calculations of α , β , γ , δ , δ' , and ϵ Plutonium, *Physical Review Letter* **2004**, in press.

New Frontiers

Each phase of plutonium has been examined computationally by beginning with a structure based on available experimentally measured parameters including bond lengths, crystal structures, magnetic moments, and others. This is done by taking a time-independent snapshot of the features of each phase. This approach is dictated to some extent by limited computer resources, even by supercomputer standards. This type of calculation is not possible today, due to both the limitations in computing resources and imperfect understanding of the many types of interactions involved.

The definitive computation might begin by computing the equilibrium configuration of α -Pu at room temperature, and then to simulate the effects of gradually heating the material and computing the time- and temperature-dependent transitions from one phase to the next. Only the properties of each atom and the quantum mechanics of the interatomic forces would be required to carry out this computation.

A New Generation of High-Performance Diffraction Gratings

Petawatt-class lasers, which deliver as much as 10^{20} watts of power onto targets in picosecond pulses, have become essential tools for studying matter under extreme conditions. In conventional laser systems, an initial low-intensity beam is amplified to greater intensity as it propagates through a lasing medium. However, extremely short (less than about 10 ps) pulses characteristic of petawatt lasers cannot be amplified to higher energies through normal amplification stages because the extreme intensities generated would damage the amplifier.

This obstacle can be overcome by sending a low-energy, ultrashort pulse through a pulse stretcher that uses diffraction gratings to change the beam-path length continuously over the spectrum of the pulse, as illustrated in Figure 1. The pulse is stretched typically by a factor of 1000, which lowers the beam intensity by the same factor and allows for safe amplification to high energies by keeping the intensity below the amplifier's damage threshold.

Once the long-pulse beam is amplified, a pulse compressor using a

second set of gratings then undoes the path-length alteration of the stretcher. It combines the spectral components to give a pulse containing all of the amplified energy in pulse duration similar to that of the initial seed pulse.

The extreme energy of the amplified pulse requires a very large beam area to avoid damage to the gratings and other optics. The large incidence angle of the pulse on the gratings exacerbates the aperture requirements. Typical designs require gratings approaching 1 meter in the long dimension. The dimension of the petawatt-class grating lines needs to be controlled to about 50 nanometers over this entire aperture. These requirements place petawatt-class compression gratings in the realm of extreme optics. Livermore is the only place in the world capable of meeting these extremely demanding requirements.

Relevance to CMS Strategic Themes

Short-pulse laser systems are used at Livermore to support materials research activities. With the extremes in manufacturing gratings and the importance of short-pulse systems in many

applications, this research is an excellent example of an activity that falls under the materials properties and performance under extreme conditions theme. This research focuses on the Laboratory's high-energy-density science and technology and the stockpile science and technology long-range plans.

Major Accomplishments in 2003

Livermore designed and manufactured gratings for petawatt-class lasers in use around the world, all of which used gold-overcoated holographic master gratings for pulse compression. However, because metal gratings absorb a small fraction of the incident laser pulse, they are limited in their ability to survive very intense pulses. Our team has been active in designing and building the equipment for an entirely new generation of diffraction gratings based on multilayer dielectric (MLD) reflectors (Figure 2). MLD gratings use constructive interference from each interface of a multilayer stack of alternating high- and low-refractive index dielectric materials, combined with a dielectric grating structure, to diffract greater than 99 percent

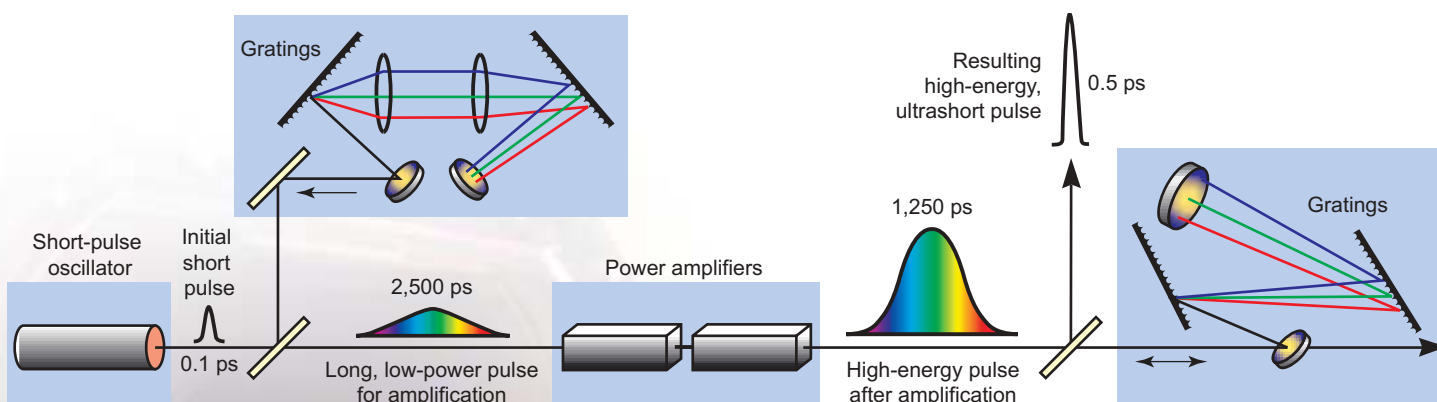


Figure 1. Diffraction gratings stretch the short initial pulse before amplification and then compress the amplified pulse back to its original width.



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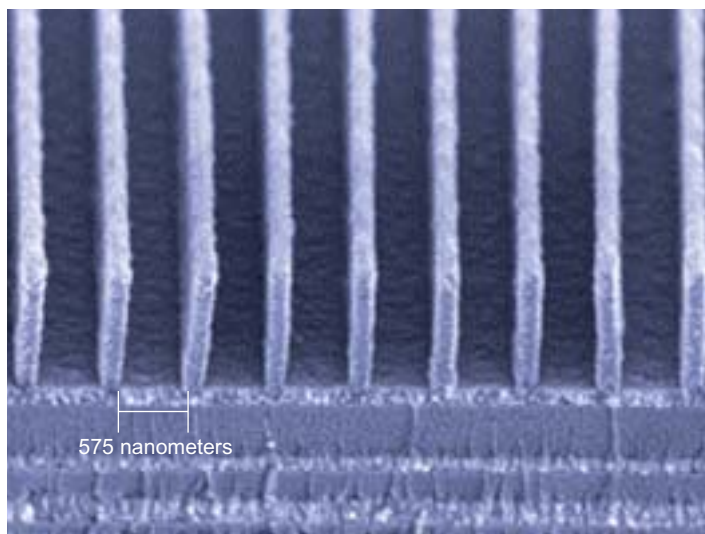


Figure 2. An image taken with a scanning electron microscope shows the fine structure of a multilayer dielectric reflection grating. The grating structure is etched into the top dielectric layer.



Figure 3. The world's largest reactive ion beam etcher was constructed in 2003. This tool can etch submicrometer grating features into substrates as large as 1 by 2 meters.

of the incident light while absorbing almost none of the laser beam energy.

Such optics are considerably more complex to fabricate than gold-overcoated materials and present extreme manufacturing challenges. First, the multilayer dielectric coating is deposited by vacuum techniques, followed by a priming step for photoresist adhesion. The next series of steps include photoresist coating and baking, exposure by laser holography, pattern development, further baking, transfer etching, and photoresist mask stripping. The optic is exposed to solvents, heat, acids, bases, vacuum, ion beams, and handling steps, each of which has the potential for damage to occur.

Each step has required significant advances in our ability to produce optical materials with greater accuracy and larger size than has ever been done before. The transfer-etching step was not possible until 2003, when we built the world's largest reactive ion mill to produce these gratings (Figure 3). This tool can etch submicrometer grating features into

substrates as large as 1 by 2 meters, about twice the size currently planned for NIF short-pulse capability.

Enabling Short-Pulse Laser Science

In addition to supplying the gratings for the world's highest-power petawatt lasers, Livermore has manufactured custom gratings for institutions around the world doing research with short-pulse lasers. They rely on the high diffraction efficiency, uniformity, and wavefront characteristics of the gratings that are possible because of our continued developments in infrastructure, design, and manufacturing. In addition to Livermore, institutions that receive these custom gratings include the Max Born and Max Planck Institutes and the Gesellschaft für Schwerionenforschung in Germany, the Laboratoire d'Optique Appliquée in France, the Rutherford Appleton Laboratory in the U.K., the Korea Advanced Institute Research Association in Japan, Los Alamos and Lawrence Berkeley national laboratories, NASA, the Naval Research Laboratory,

University of Texas, and many U.S. companies.

Related Publication

Britten, J. A. et al. Enabling Technology for Fabrication of Meter-Scale Gratings for High-Energy Petawatt Lasers, *Proceedings of the Third International Conference on Inertial Fusion Sciences and Applications*, Monterey, CA, September 7–12, 2003.

New Frontiers

We are continuing to improve our processing techniques, particularly in respect to the robustness of the multilayer coatings to deliver MLD gratings of the highest optical quality and laser damage threshold to the next generation of petawatt-class laser systems. Our unique ability to produce this essential element for petawatt-class lasers worldwide provides us with opportunities to collaborate with other facilities in this field.

Multiscale Modeling of Shock Waves

For the past several years, CMS has been collaborating with the physics department at the Massachusetts Institute of Technology to advance computer simulations of shock waves in different types of condensed media. During the past year, we demonstrated a new computational technique that allows molecular dynamics simulations to study systems for much longer time scales than previously possible. We also examined phenomena occurring when light interacts with a shock wave or shock-like modulation traveling through a photonic crystal. Our studies open many new opportunities for subsequent research in simulations and for experimental validations of the modeling predictions. We also have developed advanced “path-integral” computational techniques to investigate the vibrations of molecules under extremely high-temperature conditions (Figure 1).

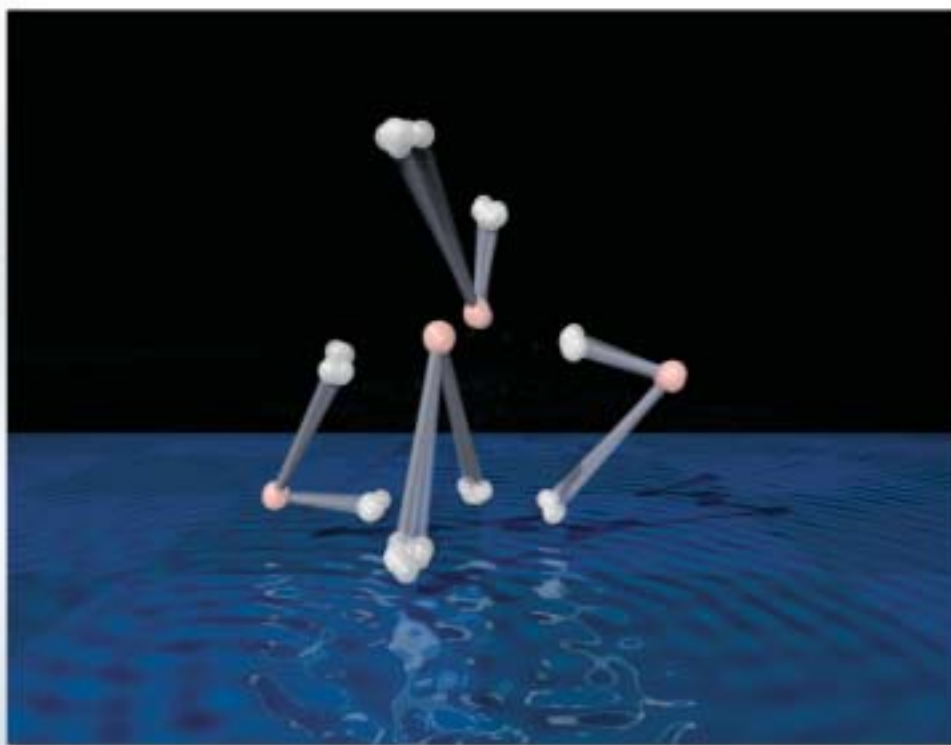
Relevance to CMS Research Themes

This project is directly related to the CMS research theme of chemistry under extreme conditions and chemical engineering in support of national-security programs. The work overlaps two Livermore long-range plan areas—stockpile science and technology and high-energy-density science and technology. The focus of this work is on simulations of shock wave phenomena and detonations in condensed phase explosives. In addition to its relevance to high explosives, the techniques are applicable to a wide range of high-density problems involving shock compression of many materials, including metals as well as explosives.

Major Accomplishments in 2003

Past molecular dynamics techniques have been limited to total elapsed times of picoseconds. It is extremely expensive to calculate forces between all simulated

Figure 1. Representation of a quantum path-integral simulation of water. The path-integral simulation couples replicas of a water molecule. Each replica is rendered as a transparent object. Quantum path integrals allow us to understand the nature of quantum effects under extremely high temperatures (up to 6000 °C).





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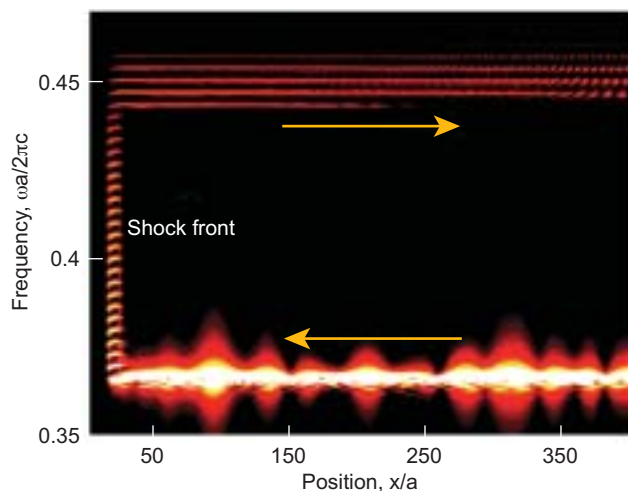


Figure 2. Simulation of a shocked photonic crystal shows that the crystal efficiently converts the frequency of light. Light enters the crystal from the right (bottom arrow) and is reflected to the right (upper arrow) by the shock front (at the left) at a higher frequency.

atoms in a fairly large system and follow each atom for a time interval along a path dictated by those forces. These difficulties are especially severe for shock waves in condensed media.

Our new multiscale technique follows only a subset of the atoms in the system and uses continuum fluid mechanics to allow the system to evolve. Using this approach, we have been able to study shock waves in solid silicon over a timescale of 5 nanoseconds, which is roughly 1000 times longer than previous simulations. The silicon compresses elastically over times of a few nanoseconds, affecting the computed shock speed. This result would not have been accessible using older techniques.

Our second computational study examined the complex environment of a shock wave traveling through a photonic crystal, which is a type of periodic dielectric medium. Sending a shock wave through a photonic crystal can convert the frequency of light (change its color) without losing energy (Figure 2). Because each photonic crystal layer has a unique index of refraction, a photonic crystal can be “tuned” so that light is changed to a specific, desired frequency. The immense flexibility offered by tunable photonic

crystals makes them possible replacements for the crystals currently used to convert light frequencies, such as the potassium dihydrogen phosphate crystals in the National Ignition Facility. Many other practical applications appear to be possible.

Future Goals

Our next step in the area of photonic crystals is to test the model predictions experimentally. Once validated, this new phenomenon can be exploited in a multitude of applications, many of which have not yet been explored. These applications include ultra-high speed communications.

Related Publications

Reed, E.J.; Soljagic, M.; Joannopoulos, J.D. Color of Shock Waves in Photonic Crystals, *Physical Review Letters* **2003**, 90, 203904.

Reed, E.J.; Fried, L.E.; Joannopoulos, J.D. A Method for Tractable Dynamical Studies of Single- and Double-Shock Compression, *Physical Review Letters* **2003**, 90, 235503.

Glaesemann, K.R.; Fried, L.E.; A Path-Integral Approach to Molecular Thermochemistry, *Journal of Chemical Physics* **2003**, 118, 1596.

New Frontiers

Continued development of new approaches to multiscale problems would allow us to carry out simultaneous simulations of long-time-scale problems with multiple embedded, shorter-timescale phenomena. A computer model might be able to adjust the coupling dynamically, as phenomena adjust to evolving environments.

We have been applying our new computational techniques to the detonation of high explosives. When high explosives detonate, there is a substantial energy release accompanying the transformation of molecules. The details of the transformation, however, are still largely unknown. We have recently found that hydrogen-transfer chemistry plays an important role as the first step in the reaction of the energetic material, nitromethane. Path-integral simulations should help to unravel the importance of quantum effects in reactions containing hydrogen. Eventually, we expect to be able to simulate the entire reaction pathway for this and other much more complex explosives.

The simulations of photonic crystals under shocked conditions also apply to other types of modulation of the dielectric medium. There may be an immense range of possible ways to modify the propagation of electromagnetic waves in such media, and the exploration of these problems experimentally, theoretically, and in simulations will be an extremely active field.

Computational Chemistry Study of the Water–Air Interface

Although water is recognized as the most fundamental and essential of all substances, remarkably little is known about its chemistry, particularly the way in which these small, triatomic molecules arrange themselves in the continuum environment of pure water and at surfaces between water and air. Over the past year, we have used computational chemistry and density functional theory to examine the chemical composition of the water–air interface. This information helps us understand a wide range of biological phenomena, including protein folding, lipid aggregation, chemical self-assembly,

and a similarly wide range of atmospheric science problems such as aerosol contributions to atmospheric fate and transport of pollutants and biological molecules, reactivity of airborne chemical weapons molecules, and many others.

Previous attempts to address the features of the water–air interface using density functional theory have been only marginally successful. Computer simulations of multi-atom substances are exceedingly time-consuming, because the absolute motions of every atom must be independently calculated at every time step, and these computational costs increase exponentially with the number of atoms in the system. At the same time, enough atoms must be included for a converged solution—one that does not change as more atoms are added to the system.

The most ambitious previous study included 32 water molecules forming a layer approximately 20 Å thick, which was found to be insufficient to establish a stable water–vapor interface. We used a larger system of 216 water molecules with a layer 35 Å thick in our study. Under these conditions, the interface was stable, and there was a region of bulk water 5–10 Å below the surface.

Relevance to CMS Strategic Themes

The long-standing challenge of understanding water in all its aspects is well suited to Livermore's strengths in chemical modeling and falls under the CMS theme area of chemical, biological, and materials science. Understanding the surface properties of water is considered an essential area of research for dealing with numerous 21st century challenges. Success in this area will impact the long-range planning areas of biological, chemical, and materials science and technology. This study is also important to environmental security and global resource management.

Major Accomplishments in 2003

We put 216 water molecules into our computer model and described all of the forces acting among them. We then solved the equations of motion for all of the atoms, allowing the molecules to evolve as the interatomic forces demand. We used both classical and quantum mechanics methods to compute the forces. Once the simulation reached dynamic equilibrium, the results were used to determine the physical and chemical characteristics of the system.

We carried out simulations on Livermore's Linux cluster, using 1440 processors in a massively parallel version of the commonly used Car–Parinello molecular dynamics code. These calculations required the equivalent of 22 complete, 24-hour days of computing spread over 6 months. The results were published in *Science*. Livermore's massively parallel computing resource allowed us to cover the whole range from the interior bulk liquid water through the transition region to the water–air surface.

The results showed a number of important features of the water–vapor interface. The water density in the bulk liquid located far from the surface was computed to be in unity as a natural result of the interatomic forces. Closer to the surface, the density decreased to zero over a distance of about 5 Å. These results provided confidence that the simulation was reproducing known features without artificial constraints.

At the surface, the majority (66%) of the water molecules were oriented with one OH bond pointed into the vapor, while another 13% had both OH bonds oriented out of the liquid. This results in a surface that is more reactive than water in the bulk liquid phase. These findings have important implications for the reactivity of aerosols and their ability to accumulate reactive species such as pollutants into solution within the

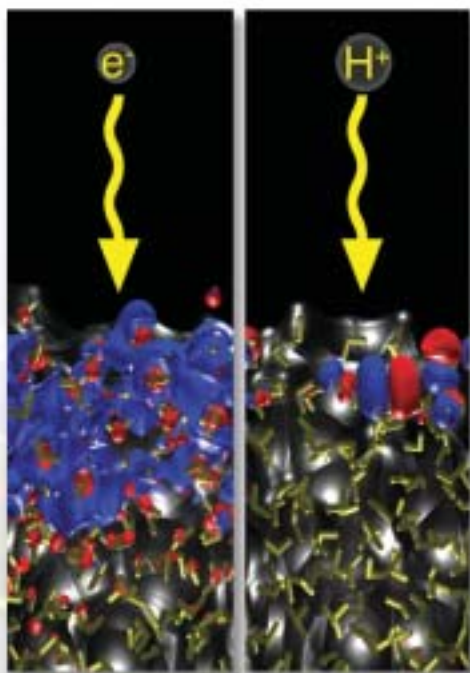


Figure 1. A massively parallel simulation shows the lowest unoccupied molecular orbital (left) and highest occupied molecular orbital (right) of aqueous liquid–vapor interface, depicting reactivity to both excess electrons and protons, respectively.



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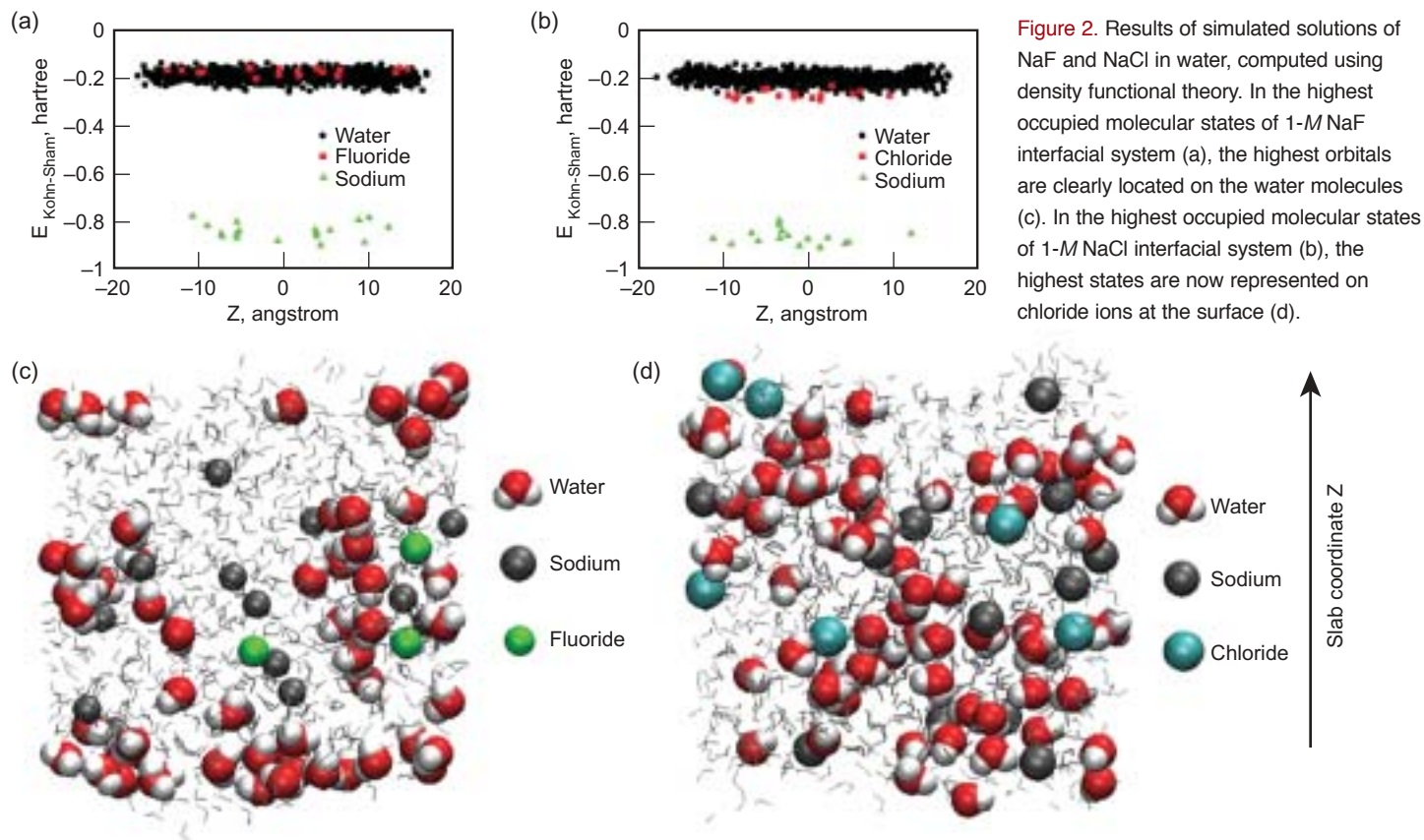


Figure 2. Results of simulated solutions of NaF and NaCl in water, computed using density functional theory. In the highest occupied molecular states of 1-M NaF interfacial system (a), the highest orbitals are clearly located on the water molecules (c). In the highest occupied molecular states of 1-M NaCl interfacial system (b), the highest states are now represented on chloride ions at the surface (d).

droplets (Figure 1). Perhaps the most important result of this study was the demonstration that the chemistry of water can be studied computationally, which opens a new area for important studies in the coming years.

Future Goals

The present simulations are the starting point for new studies related to water-vapor systems. Our focus will now be on studying the interactions of the water-vapor interface with chemical species in air pollution and Homeland Security problems, ranging from oxides of nitrogen to chemical nerve agents. We have already begun to carry out simulations in which additional chemicals

are dissolved in the water phase, changing the structure of the interface. For example, Figure 2 shows a simulation in which the presence of NaCl (salt) in water results in the chloride ions being pushed to the water surface, changing the reactivity of the surface region. In contrast, when the same amount of sodium fluoride is present in the water, the fluoride ions are more bound into the bulk water and less available to react with species in the vapor phase.

Related publications

Kuo, I.W.; Mundy, C.J. An ab initio Molecular Dynamics Study of the Aqueous Liquid-Vapor Interface, *Science* **2004**, *303*, 658–660.

New Frontiers

As capabilities in scientific computing advance, we can anticipate the ability to address problems in chemical biology, using similar computational models with immensely more powerful computers, such as the BlueGene/L with its promise of 100,000 processors. Formulating the chemistry of life in a series of computational chemistry simulations will give us enormous opportunities to solve important problems in understanding metabolism, disease, genetics, reproduction, and biological security. Using simulations to study the chemistry of water is just the first step in using these techniques to study an infinite variety of systems.

Chemical Kinetics of Hydrocarbon Ignition

In the past few years, a new type of internal combustion engine has been developed that has characteristics of both the spark-ignited (SI) engine and the diesel engine. This engine, called the homogenous charge compression ignition (HCCI) engine, operates entirely on vaporized fuels, avoiding the soot production common to the diesel engine. And because the HCCI engine runs very fuel-lean, it doesn't produce oxides of nitrogen, the other major automotive pollution source in both SI and diesel engines. HCCI combustion is dominated by chemical kinetics of ignition.

Livermore's chemical kinetic models are used worldwide by every engine manufacturer and university research group studying HCCI combustion.

There are two major reaction pathways leading to ignition. One path at gas temperatures above 1100 K is dominated by the single reaction, $H + O_2 \rightarrow O + OH$,

providing chain branching for the combustion system. This single step controls the chemistry of flame propagation and extinction and hydrocarbon detonations in the gas phase.

We have found that a different, considerably more complex reaction sequence controls ignition at temperatures below 1100 K, where most ignition events originate. This reaction is the thermal decomposition of hydrogen peroxide, $H_2O_2 \rightarrow OH + OH$, which provides the chain branching for ignition. Our modeling studies have demonstrated that this single reaction is responsible for numerous combustion phenomena—including engine knock (Figure 1) and octane number in SI engines, ignition and cetane number in diesel engines, as well as ignition in many other combustion systems, such as the laboratory rapid compression machine and pulse combustors. This reaction also determines

ignition in the HCCI engine. We have been able to use this fundamental chemical kinetic information to understand HCCI combustion and begin to develop control strategies for this new family of engines.

Relevance to CMS Strategic Themes

Chemically reactive systems and chemical kinetics are important in many Livermore programs, including the high explosives in nuclear weapons, toxics, and chemical warfare agents in chemical warfare systems. This activity is included in the CMS strategic theme of chemistry under extreme conditions.

Major Accomplishments in 2003

We developed an integrated engine simulation technique to combine our extremely detailed hydrocarbon kinetic models with multidimensional fluid mechanics models for the engine. This composite model accurately describes all of the important quantities observed in HCCI engine operations and has become the industry standard for simulations of HCCI combustion. The model couples the large physical scale of the entire engine, over which the majority of the heat release and power production occurs, with the very thin thermal boundary layer that is responsible for the hydrocarbon emissions.

We found that the only major pollutant emissions from HCCI engines are carbon monoxide and unburned fuel from boundary layers that are along engine chamber walls and in piston ring crevices. The temperatures in boundary layers are low enough that the fuel consumption rate is quite low, so the fuel in those regions is incompletely consumed, as illustrated in Figure 2. The amount of unburned fuel in the boundary layers can be reduced by operating the engine at a higher fuel concentration, which leads to higher temperatures and faster reaction. However, this increase in combustion temperatures also leads to



Figure 1. Engine piston subjected to extended operation under knocking conditions shows tremendous damage. Lower temperature combustion would reduce nitrogen oxide emissions and protect the engine from the harmful effects of autoignition and knocking.



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high production and emissions of oxides of nitrogen. These results suggest that post-combustion treatment by catalysts will be required to eliminate the high emissions of carbon monoxide and unburned hydrocarbons.

Future Goals

Our goal is to provide computational reaction models for practical fuels, particularly gasoline and diesel fuels, for use in HCCI simulations. An attractive feature of HCCI combustion is that it is remarkably fuel-flexible and can use natural gas, diesel fuel, gasoline, alcohol or other oxygenated fuels. While we have previously developed kinetic models for natural gas and alcohol fuels such as methanol and ethanol, both gasoline and diesel fuels are enormously complex mixtures of hundreds or even thousands of distinct chemical components. These include aromatic, olefinic, cycloparaffin, and paraffin species, many of which have never been modeled in the same manner.

We are developing the methodology to represent all of these constituents in fuels in an efficient, complete way. At present, we can represent both gasoline

and diesel fuels by selecting appropriate mixtures of about ten specific chemicals for which we have kinetic models. These fuels include iso-octane, n-heptane, toluene, methyl cyclohexane, 1-pentane, and a few others, but further modeling comparisons with test-engine experiments are still in progress, and kinetic models for cycloparaffins and aromatics are not yet as well developed as needed.

Related publications

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Mueller, C., et al. Effects of Oxygenates on Soot Processes in DI Diesel Engines: Experiments and Numerical Simulations, *Society of Automotive Engineers publication*, **2003**, SAE-2003-0193.

Flowers, D.; Aceves, S.; Westbrook, C.K.; Smith, J.R.; Dibble, R. Detailed Chemical Kinetic Simulation of Natural Gas HCCI Combustion: Gas Composition Effects and Investigation of Control Strategies, *ASME Journal of Engineering for Gas Turbines and Power* **2001**, 123, 433–439.

New Frontiers

Most HCCI research and development is taking place for applications in the transportation industry. Ironically, this may be the most challenging application for HCCI combustion. In particular, the need to provide for the wide ranges of engine speeds and loads which are characteristic of transportation applications appears to be very difficult without a transition to conventional SI operation at the higher levels of load required for acceleration and climbing steep hills. HCCI engines may be more suited for non-transportation applications such as stationary power production, pipeline pumping, and others. Under these environments, optimal engine conditions can be determined and exhaust catalysts can be employed to complete fuel oxidation and keep emissions extremely low. An HCCI engine for this type of application could operate with natural gas, gasoline, diesel fuel, or other special use fuel, and Livermore's kinetic models would be used to describe the ignition kinetics for any of the chosen fuels.

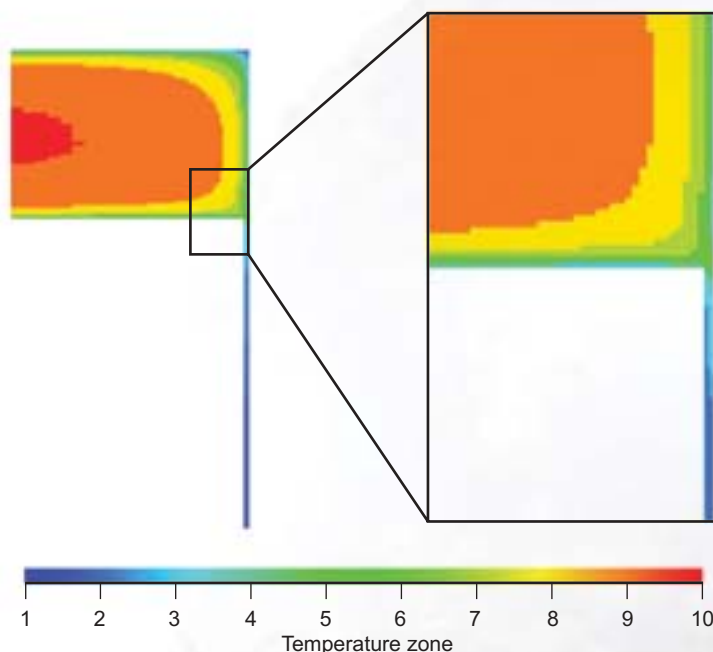


Figure 2. Schematic of an HCCI engine, showing temperatures in selected regions within the engine.

Livermore Joins OPCW-Certified Laboratories

In February 2003, the International Organization for the Prohibition of Chemical Weapons (OPCW) certified Livermore's Forensic Science Center (FSC) to support OPCW's chemical weapons inspections. This certification marked the successful completion of three years of qualification by FSC chemists to become the second U.S. laboratory supporting the OPCW, along with the U.S. Army Edgewood Center in Maryland. Fourteen other international laboratories also support the OPCW, whose major purpose is to test chemical samples collected from chemical plants and other sites to determine whether the samples contain evidence of chemical weapons.

In addition to chemical warfare (CW) agents, OPCW laboratories also look for chemicals that are precursors made during CW agent production and for chemicals that result from environmental degradation of CW chemicals. All of the OPCW laboratories around the world,

including the FSC at Livermore, carry out extremely demanding trials each year, analyzing complex mixtures of unknown chemicals. Some of the chemicals are intentionally designed to resemble actual CW agents to test a laboratory's accuracy. Successful identification of the contents of these trial mixtures is required for continued certification by the OPCW.

Relevance to CMS Research Themes

The FSC is supporting major programmatic efforts in the analysis and characterization of chemical weapons and in thwarting their proliferation. This, in turn, benefits from the science activities that originate in the CMS research theme of science in support of national objectives at the intersection of chemistry, materials science, and biology. In the future, such program activities will also be enhanced through Livermore's long-range plans in the areas of (1) biological, chemical, and materials science and

technology and (2) nuclear, radiological, and astrophysical science and technology.

Major Accomplishments in 2003

During the past year, we successfully identified the contents of samples provided to us from chemical plants and other sites. OPCW laboratories must complete analysis and submit a report within 15 days of receiving the test samples. Actual chemical warfare agents at very dilute concentrations—along with agent precursors, degradation products, and additional chemicals—are sometimes included in the samples to test a laboratory's accuracy (Figures 1 and 2).

For example, during the 12th OPCW proficiency test, our team received a complex test sample originating from an "organic waste container." This sample was spiked with two chemical weapons compounds and dibutyl-dithiophosphoramidic acid diethyl ester, a red herring. We were able to correctly



Figure 1. Example of OPCW samples received by Livermore's Forensic Science Center for analysis. Test samples occasionally contain emulsions of different layers, with each layer potentially containing suspected chemical warfare agents, precursors, or decontamination products.

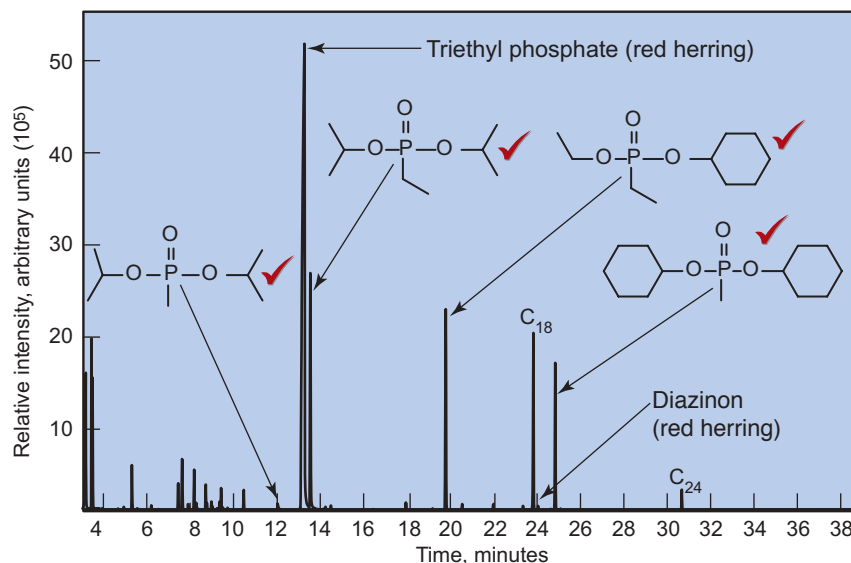
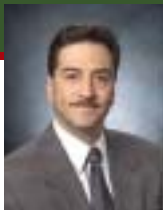


Figure 2. Chromatograph of a sample reveals the presence of a compound that is a precursor to a chemical warfare agent. Compounds indicated by a red checkmark are on the list of reportable compounds that must be identified.



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identify this red herring by using our wide range of analytical and synthesis capabilities. The analytical capabilities include gas chromatography–mass spectrometry (GC–MS), GC–atomic emission detection, GC–flame photometric detector, GC–infrared spectroscopy, GC–chemiluminescence, inductively coupled plasma, capillary electrophoresis, and nuclear magnetic resonance.

We first run simple tests to identify elements common to many CW chemicals, such as phosphorus, sulfur, nitrogen, and arsenic, and then we synthesize chemicals that we suspect are present so we can compare them to the known or authentic compound. We also derivatize sample extracts to identify chemicals that we suspect are present. Typically, derivatization chemically alters polar organic compounds, making them gas chromatograph–amenable. However, during the 13th OPCW test, a water sample spiked with 2-(N, N-diethylamino) ethanesulfonic acid and trimethyl silylation, the most commonly used derivatization reagent, produced an unstable derivatized product which eludes its detection (Figure 3). For this reason, we use various derivatization reagents to compare the known with the authentic compound.

Although two different techniques must be used to identify and confirm each reportable chemical, the FSC tries to obtain confirmation with three or four analytical techniques, since reporting a chemical that does not meet the criteria defined by the Chemical Weapons Convention Treaty would result in a failure grade in the OPCW proficiency test.

Our unique variety of analytical tools is a particular strength of the FSC and makes us a leader in this field.

Future Goals

Our goal is to continue to improve the FSC's analytical skills and tools.

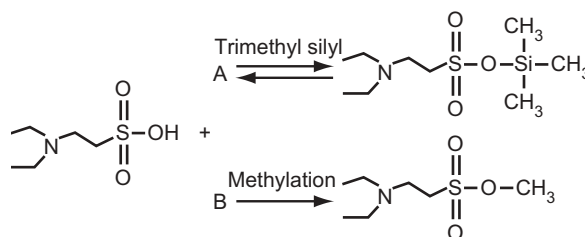


Figure 3. During an OPCW test, 2-(N, N-diethylamino) ethanesulfonic acid was spiked in a test sample. It forms a water-sensitive, unstable trimethyl silyl derivative that reverts back to the ethanesulfonic acid form (reaction A) within a couple hours, making it undetectable by gas chromatography techniques. However, methylation with diazomethane (reaction B) produces a stable derivatized product that can be detected by gas chromatography–flame photometric detector and identified by gas chromatography–mass spectrometry.

One of our technological advances involves miniaturization and portability of analytical instrumentation. Technologies such as microchips, nanotechnology, and microsensor arrays are permitting the manufacture of smaller instruments with more sensitive and faster analyses, using smaller sample volumes and low reagent consumption. The issue of chemical sensitivity is particularly important in OPCW activities, because any CW agent and its precursors and byproducts are likely to be present under extremely large dilutions. Picking the identities of small trace chemicals out of the complex background makes such tasks very demanding.

Perhaps the most significant advances are in developing miniaturized GC–MS systems for field-based applications such as on-site analysis of CW agents. This would enable real-time processing of samples and allow decisions to be made at the scene. Forensic science will benefit from our research to produce high-performance portable equipment, and the OPCW, Department of Homeland Security, and law enforcement can capitalize on such advances.

New Frontiers

OPCW's goal is to reduce and eventually eliminate CW agents. In the near future, the OPCW will begin sending samples obtained in the field under suspect conditions, and the OPCW team in the FSC must be fully prepared. Success in accurately identifying the test samples is a necessary prerequisite to assuring our capabilities. We must assume that actual field samples will present unexpected challenges, and our flexibility and broad capabilities will again be tested.

The qualification of Livermore's FSC as a certified OPCW laboratory provides credibility that will be valuable in other ways. The U.S. government and law enforcement agencies can call upon the FSC for analysis beyond the capabilities of routine forensic analytical laboratories and for interpreting samples demanding unusually high-quality forensic analysis. For example, the FSC is working to support the Federal Bureau of Investigation in the area of weapons of mass destruction materials forensics.

Studies of Protein Folding Kinetics

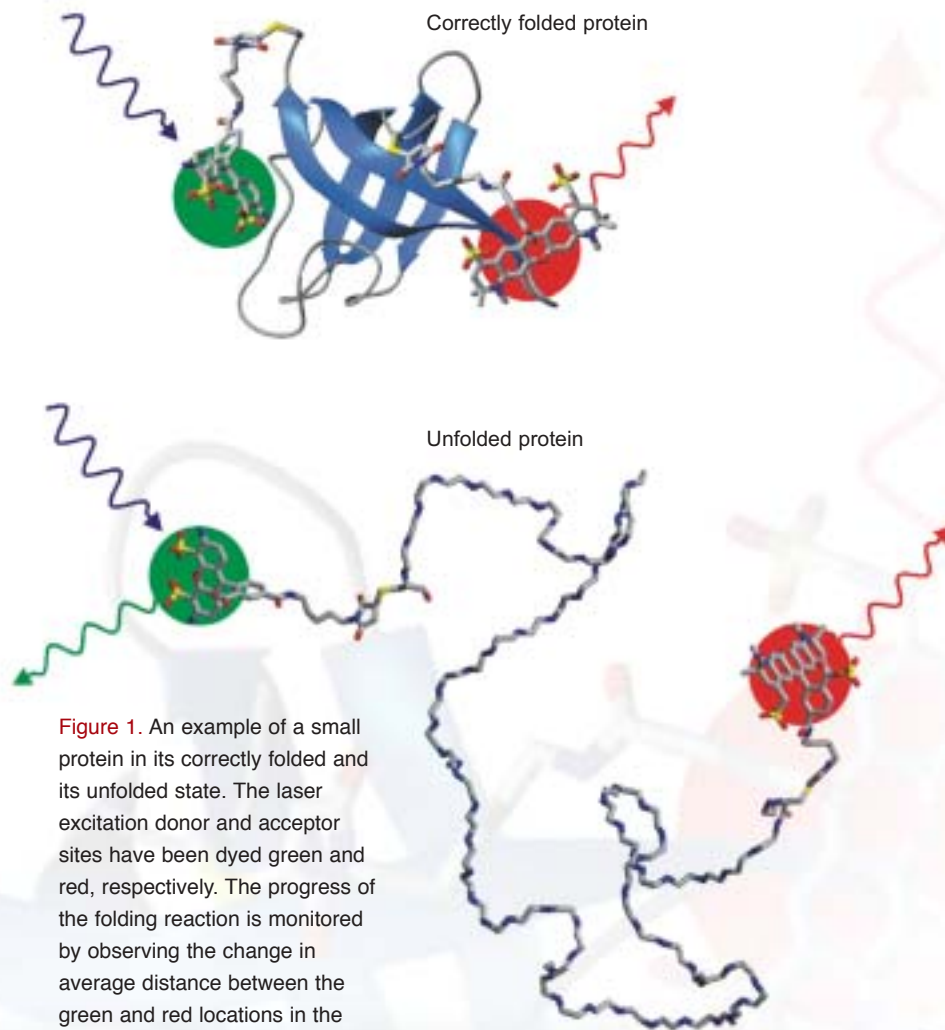
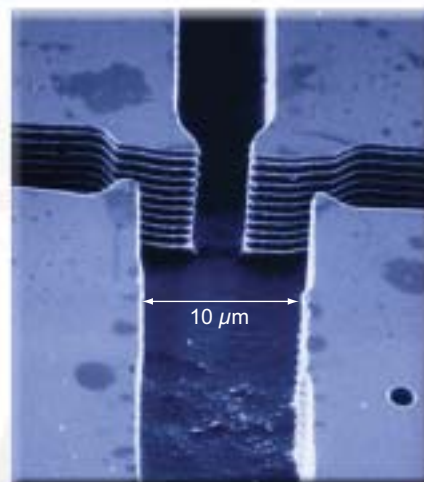


Figure 1. An example of a small protein in its correctly folded and its unfolded state. The laser excitation donor and acceptor sites have been dyed green and red, respectively. The progress of the folding reaction is monitored by observing the change in average distance between the green and red locations in the protein, which changes upon folding.

Proteins consist of chains of amino acids. Like shoelaces, they loop around each other, or fold, in a variety of ways. As with a shoelace, only one of these ways allows the protein to function properly. A misfolded protein can poison the surrounding cells, leading to diseases such as Alzheimer's, Mad Cow, and some cancers (Figure 1). Understanding mechanisms by which proteins assume their biologically active structures requires a detailed knowledge of the sequence of conformational events that lead from a denatured, random coil to a unique, native protein.

We are designing microfluidic mixers that will help us elucidate the mechanisms of protein folding. Our goal is to fabricate devices compatible with various spectroscopic observation methods that will initiate protein-folding reactions quickly while using tiny amounts of sample. In these devices, the protein-folding reaction is triggered by rapid mixing of a chemically denatured protein solution with a buffer to dilute the denaturant, the chemical agent that prevents the protein from folding. The folding reaction is observed by





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monitoring spectroscopic changes of the molecules. Using these mixers, we have, for the first time, observed the folding process under non-equilibrium conditions with single-molecule resolution. This advancement has opened new possibilities for studying intermediate and short-lived states in the folding process.

Relevance to CMS Research Themes

Our work focuses on understanding the structure of proteins, which is one of the most interesting, complex, and interdisciplinary areas in modern bioscience. This research coincides with Livermore's long-range planning in the area of biological, chemical, and materials science with potential applications in disease detection and mitigation. Most importantly, our research will advance human health by providing insight on many diseases that currently affect millions of people.

Major Accomplishments in 2003

In collaboration with scientists from the National Institutes of Health, we performed the first single-molecule measurements ever done under non-

equilibrium conditions, using our single-molecule mixer. Our data on folding and unfolding agree with bulk measurements and are similar qualitatively to those obtained in previous equilibrium measurements. In our data, we were able to isolate a short-lived, interim state between the unfolded and folded phase—the collapsed state. Results of this work were published in *Science*. We have also designed and characterized a mixer that mixes in less than 10 μs , which is the fastest mixing demonstrated to date, as illustrated in Figure 2.

Future Goals

Currently, we are working with the molecules of a protein string at the ends. We plan to insert donor/emitter dye molecules into different areas of the protein strings for a better understanding of how various parts of the protein string fold. We will also look at the proteins whose chains have been altered to determine how these alterations change the folding rates. For these experiments, we are planning to use both our single-molecule mixers and fast mixers,

collaborating with researchers at UCLA. The hope is that, given a sequence of amino acids and the environment, researchers will eventually be able to predict not only a protein's final shape, but also how it got there.

Related Publications

Lipman, E.; Schuler, B.; Bakajin, O.; Eaton, W. Microfabricated Mixer for Time-Resolved Single-Molecule Protein Folding, *Science* **2003**, *301*, 1233–1235.

Hertzog, D.; Santiago, J.; Bakajin, O. Microsecond Mixing for Protein-Folding Applications. In *Micro Total Analysis Systems Proceedings*; Transducers Research Foundation: Cleveland, **2003**, 891–894.

New Frontiers

Our main challenge is to follow one protein molecule from its unfolded to its folded state, with time resolution of microseconds or better. Ideally, we would measure naturally occurring proteins that do not contain any dye labels and avoid months of preparing the samples, so that many proteins can be studied efficiently. Currently, numerous technical difficulties prevent us from fully realizing this dream, but further improvements in optical techniques, as well as in mixer design and fabrication, are bringing us closer to this goal.

With new fabrication techniques, we will expand the range of wavelengths compatible with our mixers to UV and deep UV, which will allow us to observe the folding process in undyed proteins either through natural fluorescence or through synchrotron radiation circular dichroism measurements. Developments in microfluidics will lead to one mixer device that could be used for all applications.

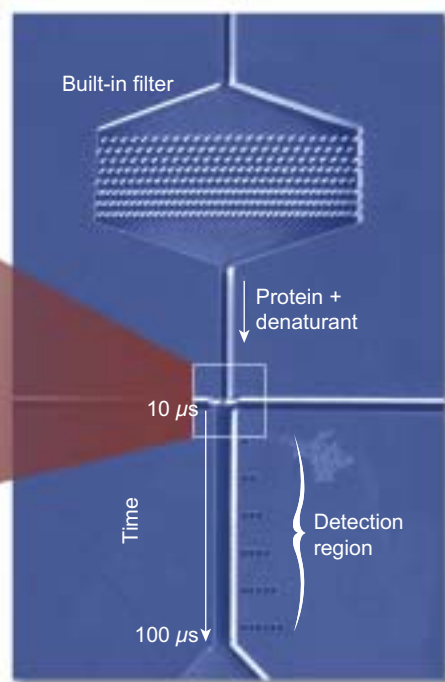


Figure 2. A schematic of a fast-flow mixer and its scanning electron micrograph (inset) show the intersection of the channel bringing the protein and denaturant from the top, with the buffer flows from the sides and the detection/observation region in the foreground. The width of the detection channel is approximately 10 μm , although the width of the protein stream is less than 1 μm , surrounded by a co-flowing buffer solution.

Single-Molecule Science: Conjugated Polymers

Conjugated polymers are a new class of electroluminescent material that promises to have a great impact in many applications, including biology and electronic displays. For example, when attached to DNA, conjugated polymers funnel their excitation energy to organic dyes and increase the detection sensitivity for DNA by a factor of 100.

Experiments with individual polymer molecules have recently led to the discovery of intermittent fluorescence emission, an unexpected behavior for

long-chain molecules consisting of hundreds of fluorescing units. We hypothesized that this peculiar property was dominated by the conformation, or physical arrangement of the atoms, in the conjugated polymer molecules, and the conformation could be controlled by a number of external parameters, such as solvent polarity. Understanding how polymer conformation influences their photoluminescence advances the design of devices based on these materials and will ultimately lead to better performance and lower power consumption of electroluminescent displays.

Relevance to CMS Research Themes

This project involves a range of scientific capabilities, including single-molecule detection and diagnostics, interactions of radiation with materials, and energy transfer within polymeric molecules. In addition to applications in energy conservation, this technology has exciting potential applications to biomedical problems as a tracer of biochemical reaction pathways. As such, this work aligns well with the CMS strategic theme of science at the intersection of chemistry, materials science, and biology.

Major Accomplishments in 2003

We demonstrated that when a single polymer molecule adopts a tightly coiled conformation in a non-favorable solvent, intra-molecular energy transfer is much stronger. Our experiments were based on monitoring the quantum-optical properties of single fluorescent molecules.

Individual polymer molecules were prepared in solutions with a polar solvent (chloroform) and a non-polar solvent (toluene) and transferred to a glass surface. The photophysical properties of single polymer molecules exhibited drastic

differences when prepared under different solvent conditions. Their spectroscopic properties as well as their emission intensity depended on the conformation of these molecules in solution.

Polymers dissolved in polar solvents showed fluorescent emission from the hundreds of independent units in the polymer. Within a single polymer molecule, energy can be efficiently transferred only when the individual units are well aligned with respect to each other. This is not the case for unraveled polymer chains as obtained from polar solvent. Since they cannot transfer energy efficiently to other portions of the polymer chain, these polymers produce emission from many fluorescent units of the polymer chain.

However, the same conjugated polymers prepared with the non-polar solvent produce emission from only two or three distinct sites within the very large molecule. Even though the polymer molecule contains hundreds of units that could otherwise emit fluorescent light, when the polymer is tightly coiled as a result of the non-favorable solvent, only a small fraction of these are actually active and emit photons. All of the other parts of the polymer apparently collect energy and funnel it efficiently to the few active units.

This work established a connection between the conformation of the conjugated polymer and its quantum-optical behavior, demonstrating that the conjugated polymer in its tightly coiled form has only two or three discrete emitter sites, in contrast to the classical photon emission from multiple emitter sites in the unfolded conformation.

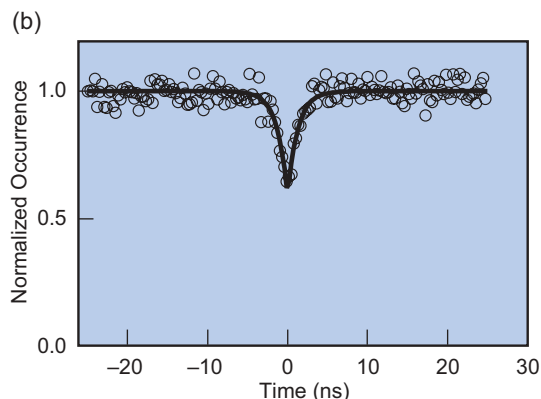
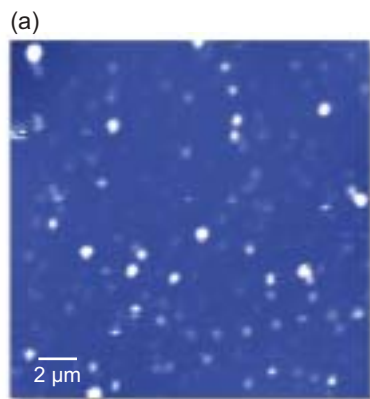
Future Goals

We will continue our studies to understand the fundamental factors

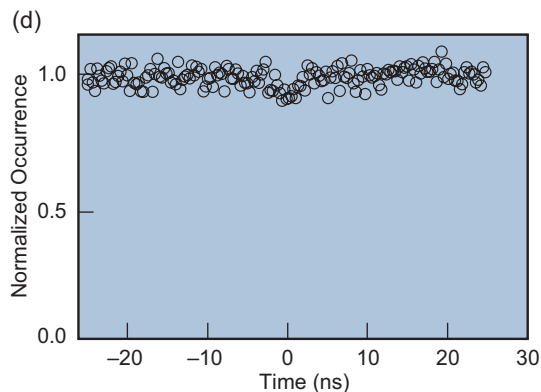
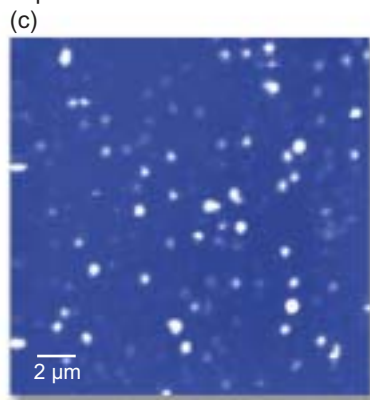


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In non-polar solvent



In polar solvent



Comparison between conjugated polymers prepared from a toluene solution (a and b) and from a chloroform solution (c and d) shows drastically different photophysical properties. Frames (a) and (c) are confocal fluorescence micrographs of individual conjugated polymer molecules (bright spots) on a glass surface. Frames (b) and (d) are photon-pair, arrival-time histograms from the two samples. The dip at time zero in frame (b) indicates that energy is being transferred from most of the molecule and emitted from only two or three active fluorescent units. The absence of the dip in frame (d) indicates fluorescence from many fluorescent units.

controlling the behavior of conjugated polymers, particularly the possibility of controlling the number of fluorescing sites by using solvents of different polarity and any other factors with comparable properties. We expect that different types of molecules are likely to have different operating properties, and methods of controlling their properties may vary widely from one group of polymers to another. Each of these will need thorough examination and development. Our goal is to develop electro-optical systems based on conjugated polymers that can be easily manipulated for multiple types of applications.

Related publications

Huser, T.; Yan, M.; Rothberg, L.J. Single-Chain Spectroscopy of Conformational Dependence of Conjugated Polymer Photophysics. *Proceedings of the National Academy of Sciences of the United States of America* **2000**, 97(21), 11187–11191.

Huser, T.; Yan, M. Solvent-Related Conformational Changes and Aggregation of Conjugated Polymers Studied by Single-Molecule Fluorescence Spectroscopy. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, 144(1), 43–51.

Hollars, C.W.; Lane, S.M.; Huser, T. Controlled Non-Classical Photon Emission from Single Conjugated Polymer Molecules. *Chemical Physics Letters* **2003**, 370(3–4), 393–398.

New Frontiers

Our studies of individual, conjugated polymers shed light on the processes that have led to the extremely high efficiency of energy transfer within a polymer molecule. The same processes are also at work when excitation energy from a conjugated polymer is transferred to a fluorescently tagged antibody that is specific for prion proteins, such as those responsible for Mad Cow disease or Parkinson's disease.

By combining these technologies, we hope to solve the mystery of how prions are transported from the digestive system to the brain. The most logical pathway is through the bloodstream, but no prions have yet been detected in the blood of infected animals. We hope to increase the detection sensitivity for prions in blood samples, which could lead to a new test for pre-symptomatic disease detection for prion diseases. Our work has led to a new grant from the Department of Defense to detect prions using the same techniques.

Probing Pathogens with High-Resolution Atomic Force Microscopy

Despite decades of study, many of the structural properties of human pathogens, including viruses, bacteria, and bacterial spores, are understood only on a rudimentary level. Fundamental understanding of pathogen structures and properties is the key to developing vaccines and detection systems in medicine and biodefense. However, common analysis tools such as x-ray crystallography or cryo-electron microscopy-based image reconstruction often cannot be applied because of the large size, heterogeneity, and lack of symmetry of human pathogens.

One method that has proven successful in imaging the intact structures of pathogens is atomic force microscopy (AFM). In this method, an ultrasharp tip is used to scan across the surface of a sample. The resulting interactions between atoms on the surface of the sample and those on the tip are measured and utilized to construct a high-resolution topographic image of the surface. AFM helps scientists determine the structure and interactions of spores, viruses, proteins, and DNA.

Relevance to CMS Research Themes

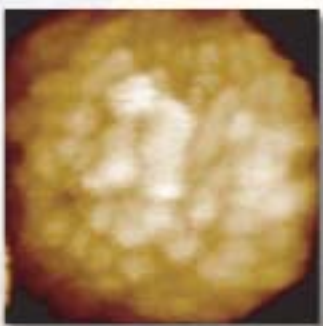
Obtaining structural information for large human pathogens provides a comprehensive understanding of pathogenesis on a molecular level. In our research, we focus on several pathogens that are laboratory models for today's most significant bioterrorist threats.

This project advances the development in pathogen signatures, which is necessary for the Laboratory's national-security mission. It also provides fundamental information for the delineation and modeling of pathogen architectures, thus advancing structural biology and medical pathology.

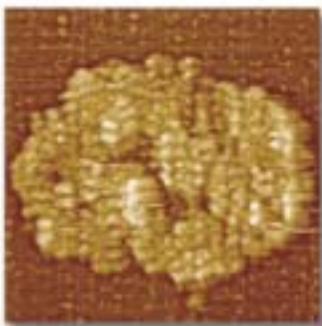
Major Accomplishments in 2003

Using high-resolution AFM, we have recently demonstrated the ability to resolve surface structures of selected pathogens to the unprecedented resolution of approximately 20 Å under physiological conditions and distinguish closely related virus families on the basis of their structural attributes. We have also examined the internal structure of pathogens by systematically peeling back successive

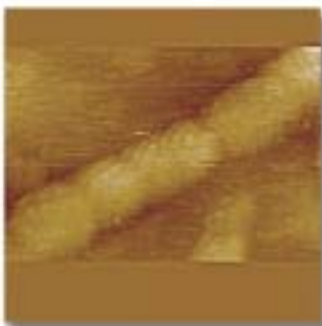
(a) 385 × 385 nm



(b) 1000 × 1000 nm



(c) 240 × 120 nm



(d) 580 × 580 nm

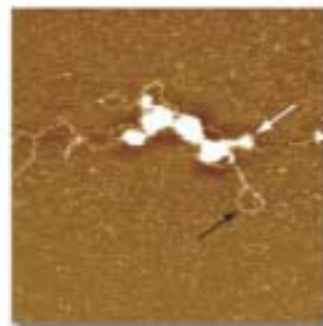


Figure 1. (a) Using high-resolution atomic force microscopy, we have imaged intact vaccinia virion, whose surface bristling with 30-nanometer protein protrusions had never been described for pox viruses. Consecutive subviral structures reveal an intact core envelope (b) and 16-nanometer linearly segmented nucleoprotein filaments (c) that contain double-stranded viral DNA (d). Tubular segments associated with DNA strands are indicated with a white arrow, while a DNA strand is indicated with a black arrow.



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(a) 1500 × 1500 nm (b) 400 × 400 nm (c) 600 × 600 nm



Figure 2. We have imaged morphology and surface structure of *Bacillus atrophaeus* spore (a) in a fully hydrated spore under physiological conditions. Its surface consists of arrays of rodlet structures (b) that fold when dehydrated (c).

layers and using AFM to visualize the features of each layer as it is revealed.

We have imaged the architecture of several important pathogens using detergents and/or enzymes to remove one layer of internal structure at a time to show the structure of the next layer within. Figure 1 shows an example of this process for the vaccinia virion, which is a laboratory model for smallpox virus. Here we demonstrated, for the first time, that AFM visualization of intact virions and internal structures makes possible the intriguing modeling of a complex architecture of a large human virus.

Using AFM, we have also resolved coat and exosporium ultramicrostructures for several species of *Bacillus atrophaeus* spores, which are laboratory models for *Bacillus anthracis*, the causative agent of inhalation anthrax. Figure 2 illustrates how the fully hydrated spore surface of *Bacillus atrophaeus* consists of highly regular arrays of rod-like structures that fold when dehydrated. These differences can be very important, as anthrax spores survive indefinitely in the dehydrated state but act as pathogens in the hydrated form.

Future Goals

We will extend our structural studies of bacterial spores to include different preparation procedures. We plan to study the effects of targeted mutations, activation, germination, and exposure to decontamination agents and examine dynamic responses of dormant spores to

the changes in the environment during the hydration/dehydration processes. We will begin evaluating hydrophobicity of single spores by measuring the adhesion forces between the individual spore and chemically functionalized AFM probes. Our goal is to establish how morphology and structural attributes for various *Bacillus* spores, including anthrax surrogates, respond to modified species, strain, and preparation procedures.

We will also continue characterization of vaccinia virus subviral intermediates and refinement of the structural model of the virion, with the focus on the structure of the nucleoprotein complex.

Related Publications

Malkin, A.J.; McPherson, A.; Gershon, P.D. Structure of Intracellular Mature Vaccinia Virus Visualized by *in Situ* AFM. *Journal of Virology* **2003**, 77, 6332–6340.

Malkin, A.J.; Plomp, M.; McPherson, A. Unraveling of the Architecture of Human Viruses by High-Resolution Atomic Force Microscopy. In *DNA Viruses: Methods and Protocols*. (Ed. P.M. Lieberman). Methods in Molecular Biology Series. The Humana Press Inc., in press.

Malkin, A.J.; McPherson, A. Probing of Crystal Interfaces and the Structures and Dynamic Properties of Large Macromolecular Ensembles with *in Situ* Atomic Force Microscopy. In *From Solid-Liquid Interface to Nanostructure Engineering*. (Eds. X.Y. Lin and J.J. DeYoreo). Plenum/Kluwer Academic Publisher, in press.

New Frontiers

Knowledge of proteomic structures is paramount for the understanding of the life cycle of pathogens and evaluation of their physicochemical properties. In the next year, we will embark on development of AFM-based immunolabeling. Our collaborators at the Children's Hospital Oakland Research Institute are currently producing monoclonal antibodies directed against surface epitopes of bacterial spores, including anthrax near-neighbors as well as purified exosporium and spore coat fractions. We will immunolocalize and identify protein components of the pathogens visualized by AFM.

We will also initiate experiments on the identification of the components of the spore coat/exosporium fractions of bacterial spores using matrix-assisted laser desorption/ionization time of flight and Fourier transformed mass spectrometry (MS). Knowing the identities of pathogen proteins from the MS experiments in combination with AFM-based immunolabeling data will allow us to discriminate between the surface-exposed versus surface-embedded proteins. By providing a foundation for identification of proteomic structures of pathogens, this work could lead to the development of vaccines, detection systems, and assistance in decontamination efforts.

Chemical and Isotopic Characterization with the NanoSIMS

Nanometer-scale characterization is essential to breaking new ground in numerous fields, including medicine and national security. Livermore's NanoSIMS 50 is the first secondary-ion mass spectrometer (SIMS) to combine nanometer-scale spatial resolution with part-per-million ($\mu\text{g/g}$) sensitivity. The NanoSIMS can map trace element and isotope distributions in samples ranging from cancer cells to interstellar grains.

Work currently underway with the NanoSIMS includes biological materials research, biological weapons attribution, geolocation for nuclear forensics, microbial mineralization processes, molecular targeting for cancer therapy, cellular uptake of carcinogens, early earth processes leading to the development of life, and cosmochemistry. For each of these projects, the NanoSIMS yields new

insights because of its unique high sensitivity and high spatial resolution.

Relevance to CMS Research Themes

Research using the NanoSIMS contributes to programs within several CMS research themes. Our research into the chemical and isotopic nanostructure of materials lies at the intersection of chemistry, physics, biology, and materials science. Efforts in biological and nuclear forensics have the potential for significant and far-reaching contributions to the Laboratory's national-security mission. Research to determine the siting of radionuclides in tumor cells falls within the application of nuclear science for human health and promises to have a direct impact on radio-immunotherapy for cancer treatment (Figure 1). This capability will contribute to the Laboratory's science and technology long-range plan in the areas of (1) chemistry, biology, and materials and (2) nuclear, radiation, and astrophysical science.

Major Accomplishments in 2003

Since its commission in June 2003, NanoSIMS has contributed to several efforts, including a collaborative project with Stanford University to study lipid rafts—macromolecule associations found in the membrane of most eukaryotic cells. These associations appear to be fundamental to intracellular signaling. However, they cannot be studied with

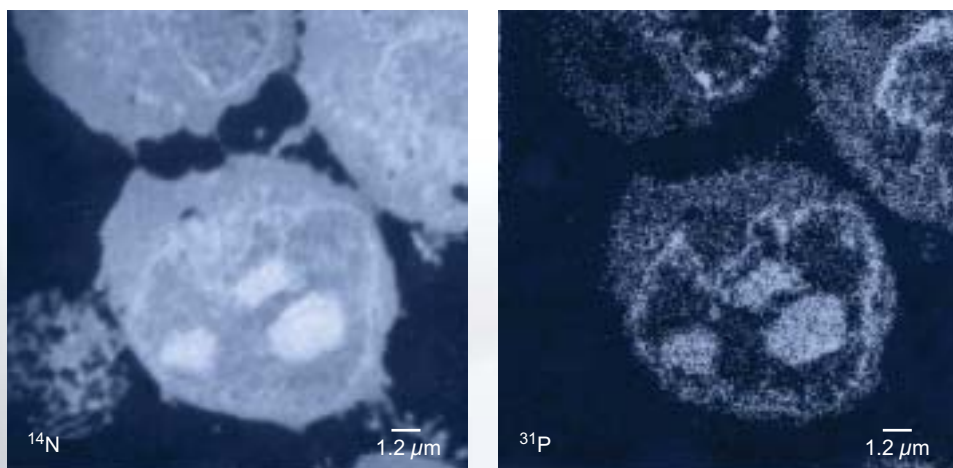
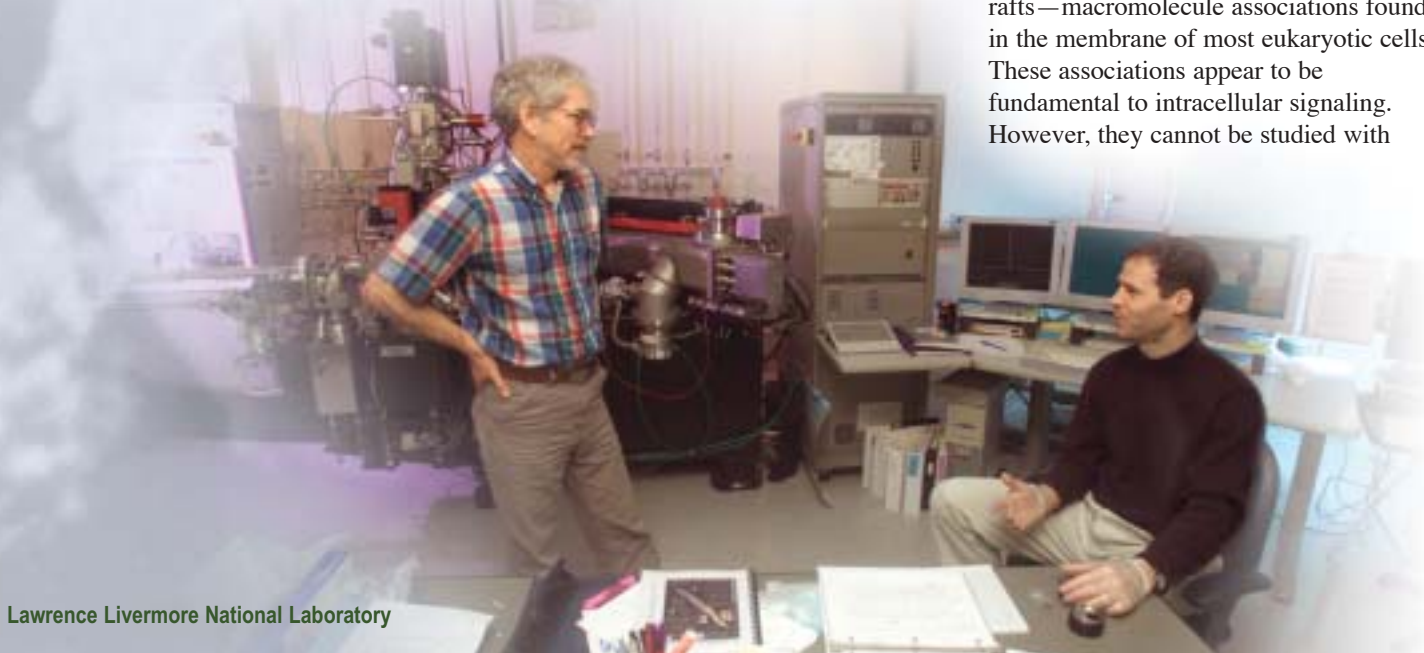


Figure 1. Nitrogen and phosphorus secondary-ion images of non-Hodgkin's lymphoma cells. The nuclear membrane can clearly be resolved in the nitrogen image and the DNA can be seen amassed along the nuclear membrane and in the nucleoli in the phosphorus image. This image has 44-nanometer, point-to-point spatial resolution.





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traditional fluorescence tagging techniques because the fluorescent molecules are large relative to the molecules of interest and might alter the lipid raft associations.

Our approach is to label the associated macromolecules with low-abundance stable isotopes (for example, ^{15}N replacing ^{14}N), which behave identically in chemical reactions. We are studying their associations in lipid bilayers on SiO_2 , which can be analyzed by NanoSIMS after freeze-drying. Our first experiments confirmed the technique using ^{15}N and ^2H labels. We are now synthesizing lipid raft components with different stable-isotope labels, for example, ^{13}C and ^{15}N , to allow us to map simultaneously the distribution of all of the membrane components to study their behavior and interactions. The insights gained by this research will have potentially far-reaching implications in the fields of biology, biophysics, biological materials, and medicine.

Livermore's NanoSIMS has already contributed to several important scientific endeavors:

- Chemical characterization of $\sim 700\text{-nm}$ inclusions in the oldest mineral on earth—a 4.4-billion-year-old zircon

- The measurement of cell-uptake of an anti-cancer drug
- Nanometer-scale characterization of bacterial spores
- Identification of $\sim 500\text{-nm}$ isotopic anomalies within interplanetary dust particles
- The analysis of presolar silicon carbide grains (Figure 2)

Future Goals

Our primary goal is to expand the application of the NanoSIMS to the full range of Laboratory programs. We have two important new initiatives focused on microbes and microbial communities. Microbes play essential roles in the formation of mineral deposits, carbon sequestration, and environmental processing of potentially harmful contaminants. Certain microbes can also be used as weapons. The NanoSIMS is the first instrument capable of resolving the trace element and isotopic composition of individual microbes (width-scale $\sim 500\text{ nm}$), opening up the potential for gaining new insight into microbial processes, as well as providing a new tool for bioforensics.

Related Publications

Amelin, Y.; Krot, A.N.; Hutcheon, I.D.; Ulyanov, A.A. Lead Isotope Ages of Chondrules and Calcium–Aluminum-Rich Inclusions, *Science* **2002**, 297, 1678–1683.

Weber, P.K.; Bacon, C.R.; Hutcheon, I.D.; Ingram, B.L.; Wooden, J.L. Ion Microprobe Measurement of Strontium Isotopes in Calcium Carbonate with Application to Salmon Otoliths, *Geochimica et Cosmochimica Acta*, in press.

Galli Marxer, C.; Park, E.S.; Weber, P.K.; Hutcheon, I.D.; Boxer, S.G. Lipid Membrane Composition Analyzed by Secondary-Ion Mass Spectrometry, **2004**, *Biophysical Journal Supplement*, 86(1), 383a.

New Frontiers

The NanoSIMS provides exciting opportunities for making important contributions in many areas. One important contribution will be in analyzing presolar materials collected from meteorites and interplanetary dust particles, which will advance our understanding of how our solar system formed. Most of the materials from which our solar system is made have been thoroughly processed and homogenized. However, small quantities of presolar dust (SiC) grains survived and have been recovered within carbonaceous chondrite meteorites.

The NanoSIMS is a new tool for studying the isotopic compositions of individual presolar SiC grains to glean new information on galactic evolution, nucleosynthesis in stars, and grain evolution in the nascent solar nebula. The ability of the NanoSIMS to measure spatially resolved isotopic ratios of carbon and nitrogen within these grains is particularly valuable, as it provides information about condensation of the SiC grains in the stellar envelope.

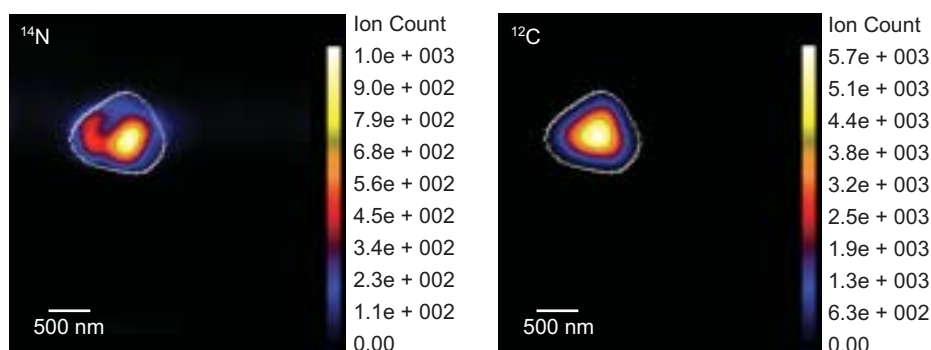


Figure 2. NanoSIMS secondary-ion images of ^{14}N (left) and ^{12}C (right) distributions in a single SiC grain from the chondritic meteorite, ALHA77307. The region of interest outlined in white shows the extent of the grain, based on the ^{12}C intensity. The distribution of nitrogen in the grain is clearly inhomogeneous and defines two sub-grains with substantially different nitrogen content. Isotopic compositions are calculated from simultaneously acquired digital images.

Discovery of Super-Heavy Elements 115 and 113

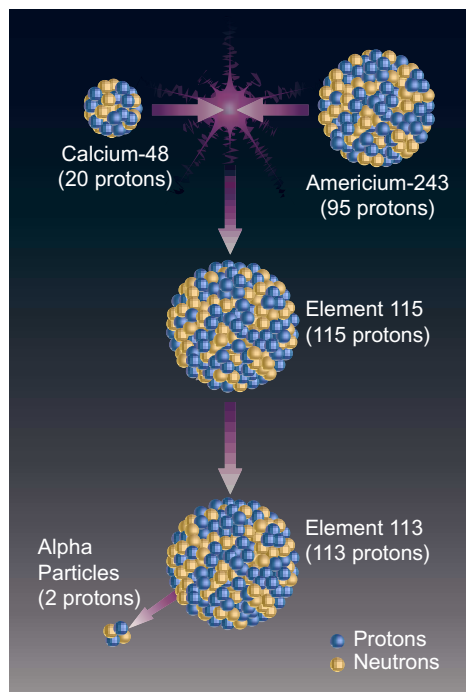


Figure 1. The fusion of an accelerated calcium-48 ion beam with an americium-243 target produces a nucleus of element 115, followed by a decay to produce a nucleus of element 113.

Livermore's partnership with the Flerov Laboratory of Nuclear Reactions at the Joint Institute for Nuclear Research in Dubna, Russia, continues to show extraordinary productivity in its synthesis of new, super-heavy elements. In 1998 and 2000, respectively, our joint experiments produced isotopes of elements 114 and 116 for the first time by using calcium-48 projectiles to irradiate targets of plutonium and curium.

In the past year, we employed the same Dubna U400 cyclotron and gas-filled recoil separator and repeated the experiments with americium-243, whose nucleus has 95 protons and 148 neutrons. The outcome of the experiments produced a new element, 115. An exciting added result was that its alpha decay generated a second, new super-heavy element, 113.

When super-heavy elements are produced, they are initially in the form of a compound-excited-state nucleus, which almost immediately loses several neutrons to form a relatively stable nucleus. Super-heavy elements are predicted to decay by losing a sequence of α particles (helium nuclei), leading eventually to the spontaneous fission of a smaller nucleus.

Relevance to CMS Research Themes

Synthesizing new elements and their isotopes and measuring their nuclear decay properties help maintain core CMS capabilities in nuclear chemistry and radiochemistry. These disciplines are essential for the fundamental understanding of the performance of nuclear explosive devices. They are also extremely valuable in providing expertise to identify and diagnose possible proliferant activities involving nuclear materials. Finally, they provide expertise in understanding issues involving nuclear power production as well as radioactive waste storage and disposal at Yucca Mountain.

Major Accomplishments in 2003

We used thin films of americium-243 as targets and an incident beam of calcium-48 ions (Figure 1) to observe four events of fusion followed by multiple α decays. Three of the events produced a virtually identical sequence of five α particles, followed by a spontaneous fission. The fourth fusion event, using a slightly higher energy of the calcium-48 beam, produced four α particles in its decay sequence, followed by a





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spontaneous fission. Its α -particle energies were larger than those observed in the first three events, and the duration of the α -decay sequence was shorter. All of these factors indicated that the first three events produced the same isotope of element 115, while the fourth event produced a different isotope of element 115. The significance of discovering two isotopes is that we gain more understanding and can map out a larger region of the chart of nuclides.

The α decay of element 115 produces element 113, as illustrated in Figure 2. As a result of two different calcium-48 energies, the decay sequences produced two isotopes of the previously unknown element 113, specifically $^{284}_{113}$ and $^{283}_{113}$. Subsequent α decays produced elements 111, meitnerium (element 109), bohrium (element 107), and finally dubnium (element 105), which is the source of the spontaneous fission that terminates each chain.

The complete reaction sequences—including the lifetimes of each intermediate state, the energies of the α particles emitted, and comparisons with previous experimental results—provide a “fingerprint” identifying the nucleus initially produced and all of the intermediate nuclei in the cascade leading

to spontaneous fission. This process led to our determination that the first three events represented the decay of $^{288}_{115}$ and daughters, while the fourth event was the decay sequence arising from $^{287}_{115}$. These long decay chains were the first recorded observations of any isotopes of elements 115 and 113.

Future Goals

We are sending a new target of californium-249 to Dubna that will be used to potentially produce element 118. This isotope would decay through elements 116 and 114 and end in spontaneous fission. We will continue to make atoms of element 115 and focus on studying the chemistry of its final α -decay sequence product, element 105 (dubnium), which has a half-life of hours or even days.

We will participate in the construction and operation of the mass analyzer of super-heavy atoms (MASHA) in Dubna, which will measure the atomic mass of the heavy atoms from our experiments and provide an independent verification of isotopes produced. The MASHA is expected to increase the production rates of super-heavy atoms from these experiments by a factor of 20 and enable us to carry out a variety of new chemical and physical measurements.

Related Publications

Oganessian, Y.T. et al. Experiments on the Synthesis of Element 115 in the Reaction $^{243}\text{Am} (^{48}\text{Ca}, xn)$ $^{291-x}115$. *Physical Review C* **2004**, 69, 021601.

Oganessian, Y.T. et al. Observation of the Decay of $^{292}116$. *Physical Review C* **2001**, 63, 1301.

New Frontiers

Our long-term goal is to confirm the existence and limits of the so-called “island of stability.” This region on the periodic chart has been predicted for many years to include massive atomic nuclei with half-lives measurable in years. In order to produce larger nuclei closer to the center of the “island,” it will be necessary to make nuclear projectiles even more enriched in neutrons than calcium-48. Since these neutron-enriched atoms are unstable themselves, they will have to be created immediately before firing them at the targets in a rare isotope accelerator (RIA). Our future experiments will take place using a new RIA that will be built at a low-energy nuclear physics facility in the United States.

By creating short-lived calcium-50 or calcium-52 for these experiments, we expect to find nuclides of elements 114–116 with half-lives of hours or days and observe first-hand the properties of elements in the “island of stability.” These experiments will provide enough new material to refine and improve theoretical models of nuclear structure and stability. Ultimately, the models will help describe and explain variations in nuclear stability and the properties of shell structures in super-heavy nuclei.

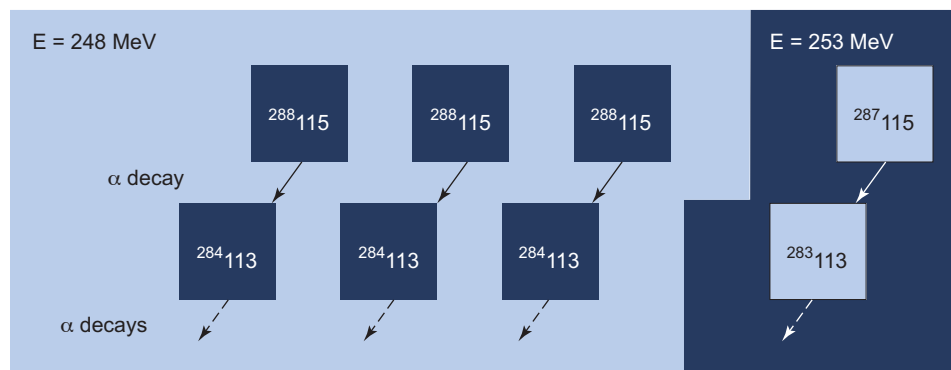


Figure 2. The reaction sequences in the decay chains of the new element, 115, indicate the presence of a second new element, 113, and its isotopes.

High-Sensitivity Gamma-Ray Imaging

Recent improvements in detector manufacture and digital signal processing have advanced the development of high-sensitivity and high-spatial-resolution, semiconductor-based gamma-ray imaging detectors. In addition to taking gamma-ray pictures, these gamma-ray imaging instruments can identify very weak, normally invisible gamma-ray sources. The high spatial resolution is derived by two-dimensional segmentation along with pulse-shape analysis. Gamma-ray tracking algorithms identify the path of gamma rays within the detector, enabling the detector to determine the source of gamma rays without the use of a collimator. These so-called Compton cameras can be realized in compact and potentially portable systems that provide omni-directional sensitivity. Figure 1

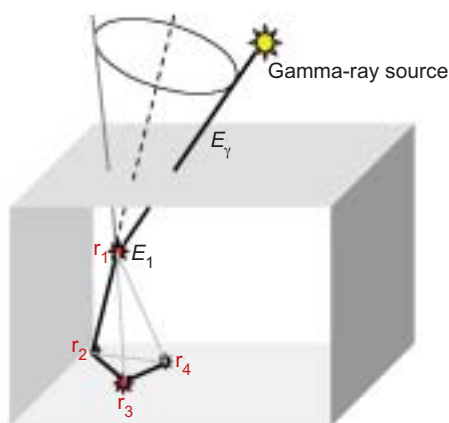


Figure 1. In a Compton imager, a gamma ray enters the detector and interacts through Compton scattering several times until it is fully stopped by the photo-electrical effect. Two-dimensional segmentation and signal processing provide energies (E) and three-dimensional positions (r) of the individual gamma-ray interactions. Gamma-ray tracking algorithms determine the scattering sequence of the interactions. Based on the Compton scattering formula, it is now possible to derive the incident angle of the gamma ray without using a collimator.

illustrates the concept of gamma-ray tracking based on Compton imaging.

Many applications for Compton imaging can be envisioned, from astrophysics to nuclear medicine and homeland security. These devices promise high sensitivity to illicit nuclear materials. They could also provide earlier detection of cancer by using radio-labeled tracers to target unique molecular characteristics of the disease.

Relevance to CMS Research Themes

The development and implementation of new or improved concepts in radiation detection is part of the applied nuclear science theme. This science area is valuable in supporting programs ranging from basic research to national health and homeland security.

This research is motivated by our desire to develop measures to counter the proliferation of nuclear materials. These instruments are able to not only image and localize a radioactive source of interest, but also identify nuclear threats in the midst of legitimate sources found in commerce and in the environment. This achievement is due to the use of high-energy-resolution semiconductor detectors, which allow isotopic identification to address false detector alarms.

In addition to thwarting illicit proliferation of nuclear materials, the detector systems can be deployed to support areas such as stockpile stewardship and nuclear safeguards and monitoring. We are also developing systems to better detect early stages of cancer, particularly breast cancer, and improve cancer treatment. Underlying concepts such as pulse-shape analysis and gamma-ray tracking are being translated into basic research such as the Majorana experiment, which is designed to measure fundamental properties of the neutrino, such as its mass.

Major Accomplishments in 2003

Over the last year, we have implemented several different Compton

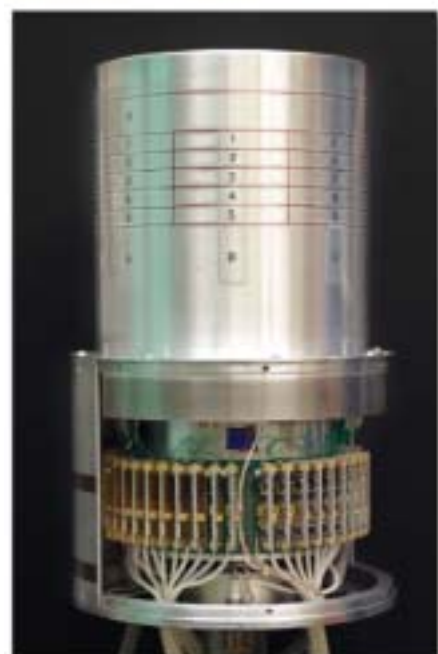


Figure 2. Two Compton camera systems consist of two-dimensionally segmented, high-purity germanium (HPGe) detectors. The unit on the top, in a planar configuration, is able to provide a position resolution of about 0.5 mm at 122 keV in all three dimensions. The bottom unit, one of the first highly segmented coaxial HPGe detector, is currently achieving a position resolution of about 4 mm in all three dimensions. Both detectors contain custom-made preamplifiers, which are characterized by their compactness, low noise, and high bandwidth.



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imaging systems (Figure 2). Using the planar configuration, we demonstrated the superior sensitivity of a Compton imaging system over a non-imaging system (Figure 3). We also demonstrated sensitivity for omni-directional gamma-ray imaging and merging gamma-ray images with visual images. In addition to the one-detector implementation in the planar configuration, we also implemented the first two-dimensionally segmented, coaxial high-purity germanium detector as a Compton imager. This instrument is characterized by its high efficiency and excellent isotope identification capabilities. It can also be used as a Compton camera.

Another system, consisting of a planar silicon and planar germanium detector, was assembled to demonstrate the ability to image gamma-ray energies from 100 keV to above 1000 keV. Extensive studies of a variety of Compton camera implementations not only indicated the

enormous gain achievable with Compton imaging systems but also showed that a system consisting of two detector materials (for example, silicon and germanium) provided the best performance for energies ranging from 100 keV to more than 1000 keV. To optimize the sensitivity of Compton cameras, we have improved the position resolution in our planar detectors down to 0.5 mm at an energy of 122 keV.

Future Goals

Our goal is to implement the next generation of Compton imaging systems, which will be characterized by larger individual detectors and an improved data-acquisition system. The fully digital data-acquisition system must be modified to handle count rates of up to 100 kHz, and more real-time processing and imaging must be implemented. We will pursue optimization of the Compton

imaging system for early cancer detection. We have started to observe three-dimensional (tomographic) gamma-ray images using one of our devices, which will become an important tool for cargo inspection or nuclear medicine. We intend to build a deployable system for homeland-security applications based on a compact and potentially portable Compton imaging system. We anticipate that this system will be ready to carry out the first field demonstrations in about two years.

Related Publications

Lee, I.Y.; Deleplanque, M.A.; Vetter, K. Developments in Large Gamma-Ray Detector Arrays, *Reports on Progress in Physics* **2003**, 66, 1095–1144.

Vetter, K. Gamma-Ray Tracking: Utilizing New Concepts in the Detection of Gamma Radiation, *European Physical Journal A* **2002**, 15, 265–269.

Acquisition time: 2 min, 1 s
Number of tracked events: 176
Number of projected events: 62

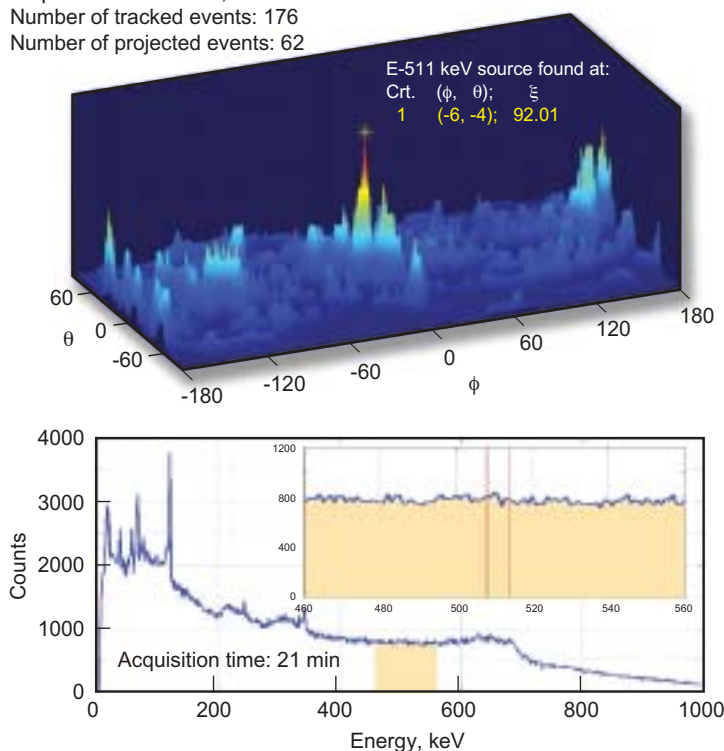


Figure 3. By employing the Compton imaging concept in an HPGe detector (top), we can recognize and localize the 511-keV gamma ray from a weak ^{22}Na radioactive source amidst a strong background of a ^{60}Co source. By contrast, a non-Compton imaging system (bottom), despite the very good energy resolution, did not distinguish the gamma-ray source.

New Frontiers

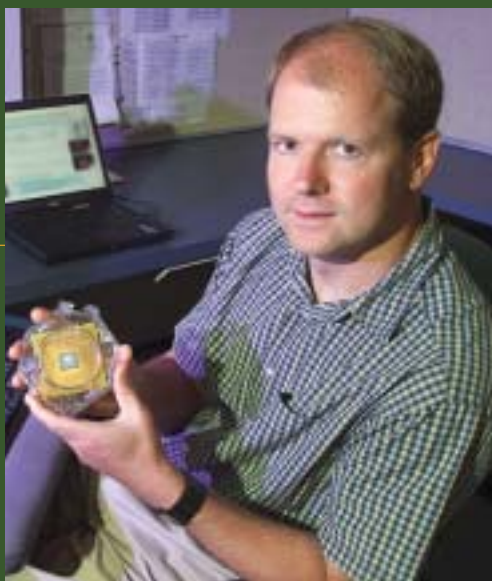
The technology we are currently developing will potentially find a wide range of applications. The development of a compact and semi-conductor-based Compton imager is being funded by the new Department of Homeland Security to provide increased sensitivity in the detection and identification of nuclear materials. We are exploring other capabilities to increase the sensitivity by either increasing the size of the systems or by implementing new features, for example, the tracking of the Compton electron or improved signal processing and imaging schemes. The development of new detector materials, such as scintillating fibers with much increased light output, will potentially allow us to build affordable large-scale imaging systems.

Chemistry and Materials Science

Directorate



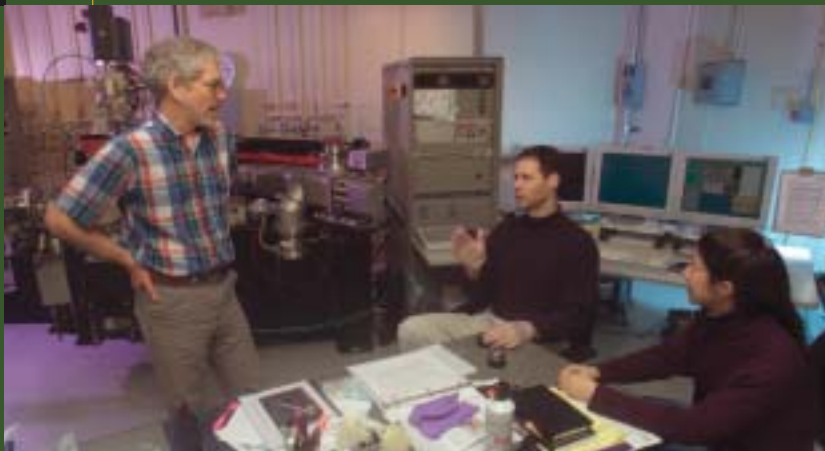
Dynamic Teams



Divisions

Centers

Institutes



Chemical Biology and Nuclear Science Division

To provide unique and integrated solutions to issues at the intersection of chemical, biological, and nuclear science and to sustain a strong life-sciences expertise

The Chemical Biology and Nuclear Science Division (CBND) conducts leading-edge research in its science disciplines while maintaining a strong focus on the challenges of Livermore national-security missions. Primary program areas include support for the U.S. Stockpile Stewardship Program, homeland security, counterproliferation, and environmental programs. The division has exceptional expertise in radiochemistry, nuclear science, forensic and isotope chemistry and spectroscopy, groundwater chemistry, biochemistry, and bioanalytical science. For example, our support for the Department of Homeland

Security focuses on capabilities in radiation imaging, dose response, nuclear attribution technologies, and air-sea-land port-of-entry protection. CBND also provides a majority of the technical staff to CMS institutes and centers, including the Glenn T. Seaborg Institute, the BioSecurity and Nanosciences Laboratory, and the Forensics Science Center (see separate articles for more details).

Strategic Theme-Related Accomplishments in 2003

CBND is aligned with the CMS research theme of *science in support of national objectives at the intersection of chemistry, biology, and materials science*. The following are highlights of CBND accomplishments:

BioAerosol Mass Spectrometer: The BioAerosol Mass Spectrometer (BAMS) facility and research group made a number of important studies during the past year. Two surrogates for *B. anthracis*, which produces anthrax, were used in the most impressive demonstration to date, establishing this technology as reliable, flexible, and analytical. Surrogates *B.*

thuringiensis and *B. atrophaeus* were reliably distinguished from a suite of other biological and nonbiological materials, including fungal spores, cigarette smoke, diesel particulate matter, and undifferentiated atmospheric air pollution. The two surrogates were also accurately distinguished from each other, even when mixed with a broad mixture of other aerosol materials. This facility has demonstrated ability comparable to a Biosafety Level-3 facility in distinguishing between different aerosols.

This work, combined with previous analyses of the effect of variations in laser power on the mass spectra, is proceeding along an extended series of further demonstrations of the BAMS technology. Plans are in place for a next-generation facility that will dramatically increase the throughput rate and its ability to detect smaller fractions of target aerosol particles.

Nevada Test Site Geochemistry: We have been studying the long-term environmental impact of underground nuclear testing at the Nevada Test Site (NTS). In particular, we are using mass spectrometry isotopic ratio measurements to investigate

Figure 1. Our team employs BioAerosol Mass Spectrometry (BAMS) systems to identify bioagents, such as anthrax, from only a single spore or cell and to clarify the molecular changes that occur in normal and cancerous cells.





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groundwater flow and radionuclide transport from underground test cavities at scales ranging from submicrometers to hundreds of kilometers. Recent CBND field, experimental, and modeling studies have demonstrated how nanoscale mineral colloids facilitate transport of actinides. Observation of colloid-facilitated transport of plutonium, first documented at NTS, has now been seen at Rocky Flats and Hanford, and it is becoming accepted as the dominant transport mechanism for low-solubility actinides. These results have led to a drilling project to re-enter an underground test cavity at NTS to recover melt glass and groundwater samples that will address questions regarding the origin of actinide-bearing colloids.

Transport Containers and Homeland Security:

The Department of Homeland Security is concerned with the potential for “dirty bombs” to be smuggled and exploded in populated areas of the U.S., dispersing highly radioactive material over a wide area. This type of material could enter the country through packaged mail or in any of the 7 million shipping

containers that arrive each year. CBND is supporting the Department of Homeland Security Radiation Detection Project to address these concerns. In a recent test of the project’s detector systems, two legal shipments of radiation source material were found among hundreds of packages at a FedEx shipping center in Denver.

Livermore is also working with the U.S. Coast Guard to provide detectors that use neutron beams to probe shipping containers. The goal is for all containers to be scanned before they are allowed into U.S. ports. This program could improve current inspection activities, where only two percent of containers are inspected.

State-of-the-Art Technologies

CBND’s Heavy Element Group produced and detected new elements 113 and 115 in a collaboration with the Joint Institute for Nuclear Research in Dubna, Russia. The discovery followed recent efforts by the same Livermore group who reported the first confirmed discoveries of elements 114 and 116, making a total of four new element discoveries for the team.

As part of the Laboratory’s focus on maintaining the security of our water supplies for agricultural and domestic uses, CBND provided leadership in a water science initiative that included study of the geochemistry and microbial controls on nitrate contamination of California groundwaters.

Many projects in bioforensics, single-biomolecule detection systematics, bio-organic synthesis, and nanobiochemistry have also been carried out within the BioSecurity and Nanosciences Laboratory. In one project, the environmental radiochemistry group studied the mobility of fission product ^{129}I and its use as a tracer of the nuclear fuel cycle. The presence of ^{129}I can be used to confirm suspected use of nuclear reactors by potentially proliferant nations, and it can also be used to identify areas with possible radioactive contaminations.

Future Goals

CBND will continue its commitment to core national-security programs at the Laboratory while promoting new basic science that anticipates future needs in chemical, biology, and nanotechnology. The division will also play an important role in the national Genomics:GTL (formerly Genomes to Life) initiative, with a focus on single-molecule, gene, and protein studies. In addition, field exercises in the next year promise to return rare samples that will allow CBND nuclear scientists to pursue a strong experimental program. CBND will also expand on its acknowledged prominence in environmental science and continue to nurture its core discipline science, tailor its facilities appropriately, and anticipate and respond to new programmatic opportunities.



Figure 2. Many of the detection technologies developed by Livermore will have significant homeland-security applications. Shown here is an adaptable radiation area monitor, housed in a nondescript briefcase during a demonstration to the secretary of the U.S. Department of Homeland Security, Tom Ridge (right).

Chemistry and Chemical Engineering Division

Science and engineering that investigate the chemical properties, reactivity, and synthesis of energetic and optical materials

The Chemistry and Chemical Engineering Division (CChED) supports major Laboratory programs and executes R&D in the chemistry and chemical engineering disciplines. The division is organized into the following program elements: energetic materials, weapon materials compatibility, and aging studies in support of the U.S. Stockpile Stewardship Program; National Ignition Facility (NIF) optics, NIF target fabrication, and NIF materials; and nonproliferation. Major scientific capabilities include extreme chemistry, high-performance computational chemistry and chemical biology, physical chemistry, synthetic chemistry and advanced material synthesis, and chemical engineering.

Strategic Theme-Related Accomplishments in 2003

CChED is aligned with the CMS research theme of *chemistry under extreme conditions and chemical engineering in support of national-security programs*. The following are highlights of CChED accomplishments:

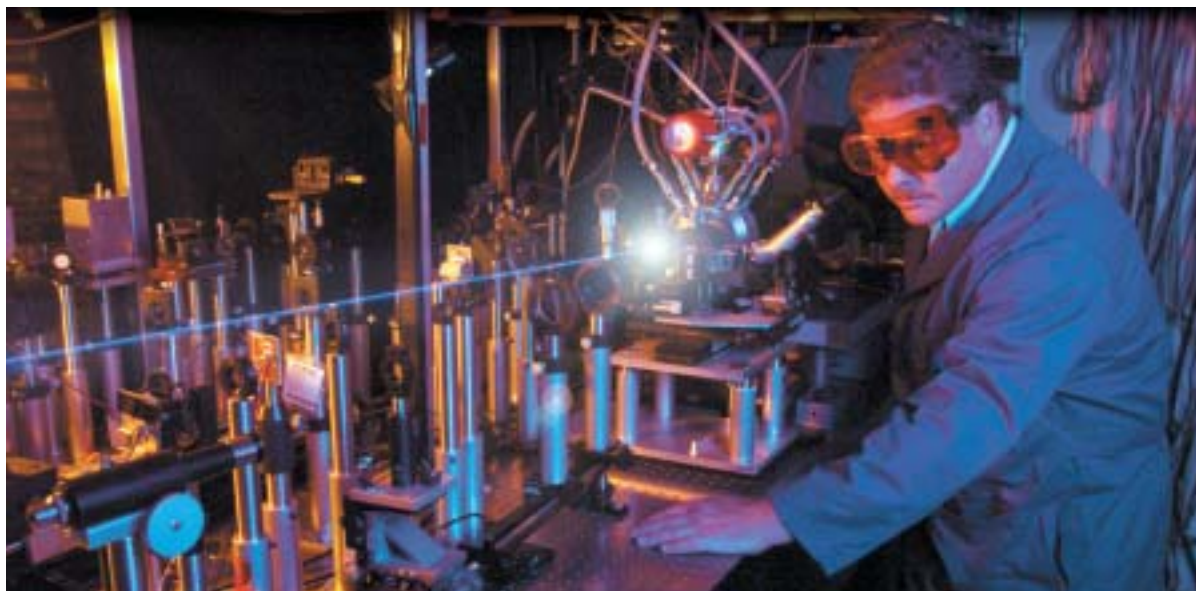
Experiments at Extreme Pressure: A major element of our research involves physical and chemical systems at extremely high pressures and temperatures—conditions found in nuclear weapons performance studies, in laser fusion experiments such as those expected in the NIF, and in planetary interiors. Extreme pressures produce unexpected phenomena. For example, in very-high-pressure, condensed-phase detonations, initiation reactions involve atom transfer within the fuel molecule, which does not further increase the already extreme pressures. However, in atmospheric-pressure, gas-phase detonations, initiation reactions usually involve breaking the fuel molecule into two or more fragments, which does increase the pressure. Our recent advances in this area have included new computational modeling techniques

and development of very demanding experimental techniques using diamond anvil cells.

We have also applied our capabilities in diamond-anvil-based experiments to measurements of elastic and vibrational properties of iron and cobalt at the highest static pressures ever studied (above 1 Mbar). These data will provide information about conditions in planetary interiors and insight into planetary formation and evolution (Figure 1). These experiments will also provide essential equation-of-state information that can be applied to weapons performance and NIF experimental design studies.

Ultra-Low-Density Aerogels: Livermore is internationally recognized for synthesizing extremely low-density materials with specialized composition. In the past year, we produced a solid-phase sample of silica with the lowest density (1 mg/cm^3) ever made for a solid (Figure 2). The production of this sample required the use of newly developed, rapid supercritical extraction processes. The ability to synthesize such materials assists Laboratory programs in materials performance, warm-dense matter, and

Figure 1. We have recorded the highest-ever ultrasonic sound velocities in a diamond anvil cell, using impulsive stimulated light-scattering techniques.





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high-energy-density physics. Recent examples of applications are an iodine-doped polystyrene material to be used as a heat pre-shield in laser-driven experiments on the Omega and NIF lasers and novel metal-doped nanocellular materials for NIF targets.

We have continued to explore the production of aerogel materials for new elements in the periodic table. Production of aerogels of urania (UO_3) and thoria (ThO_2) provide materials of importance to Livermore programs and also provide unique insights into the potential and limits of synthetic chemistry at extreme low densities. As an example, the urania aerogels have densities in the range of 0.1 to 0.2 g/cm^3 and physical features in the size range from 5 to 20 nanometers.

State-of-the-Art Technologies

Over the past years, CChED members have played large roles in developing optics manufacturing techniques for NIF, and the large crystal growth team had eight consecutive successful production runs in 2003. Better understanding of the crystallization and growth process has led to improved performance with lower levels of growth defects and

inhomogeneities to reduce bulk damage. Combined efforts of the NIF glass and advanced synthesis groups have helped the groups to characterize mechanisms of surface damage and etch pit growth and use new sol-gel coatings to design effective mitigation schemes.

Several significant achievements were made in computational chemistry. The multiscale simulations of shocks in condensed materials involving molecular dynamics and continuum fluid mechanics and the ab initio studies of the water-vapor interface are discussed in more detail in separate articles in this annual report. Other advances have been made in studies of electronic structure modeling of high explosives, chemical kinetics of chemical warfare nerve agents, modeling of aerosol chemistry, and chemical reactions in biological environments.

The Energetic Materials Program continues to carry out development of conventional and novel high explosives. Recent syntheses of composite nanocellular materials have incorporated high-Z metal ions into aerogel matrices and can now provide lightweight, high-performance materials. Other efforts have

led to a new class of nanoenergetic materials whose properties can be tailored at the micro-structural level.

Chemical engineers from CChED have held important leadership responsibilities in several programs, where they conduct foreign threat assessments of countries developing weapons of mass destruction. During recent conflicts in Afghanistan and Iraq, these individuals assumed particularly important roles.

Future Goals

Our strategic plan centers on R&D efforts in areas involving the chemistry of energetic, optical, and other high-performance materials under extreme conditions. Our capabilities in energetic materials, materials compatibility and aging, synthesis of new materials, laser optics and target fabrication, computational chemistry, and hydrodynamic modeling will continue to advance Laboratory missions that include advanced conventional weapons, stockpile stewardship, forensics of weapons of mass destruction, and the technical challenges of homeland security.

Through cross-cutting research, our scientists will advance understanding of the energy-release mechanisms of energetic materials and nanocomposites to reap the full potential of these novel materials.



Figure 2. We have successfully synthesized ultra-low-density aerogel at 1 mg/cm^3 , setting a new world record.

Materials Science and Technology Division

Providing a fundamental scientific capability for predicting the properties and performance of materials under extreme conditions

The Materials Science and Technology Division (MSTD) supports major Laboratory programs and executes world-class R&D in a wide range of disciplines. Our program elements are aligned with specific projects supporting the U.S. Stockpile Stewardship Program, the Yucca Mountain Project, and the nation's counterproliferation efforts. Important disciplinary capabilities in MSTD include metallurgy, actinide science, materials synthesis and nanobeam characterization, high-performance computational materials science, electrochemistry, ceramics, solid-state physics and chemistry, surface and interface science, and coatings and multilayered materials. Conventional-scale and nanoscale applications of all of these are being pursued.

Strategic Theme-Related Accomplishments in 2003

MSTD is aligned with the CMS research theme of *materials properties and performance under extreme conditions*. The following are highlights of MSTD accomplishments:

A major focus for MSTD has been the study of correlated *f*-electron materials

properties. This has included determination of full-zone phonon dispersion curves for δ -Pu, computational simulations of all of the atmospheric pressure phases of plutonium, and experimental observation of the spectroscopic consequences of spin and orbital moment interactions. These topics are discussed in more detail in separate articles in this annual report.

In support of the Stockpile Stewardship Program Enhanced Surveillance Campaign, we have developed and qualified material characterization procedures for the W87 and W68 "pits"—shells of plutonium that play a key role in the performance of a nuclear weapon. We also completed fundamental studies of pit lifetimes, which will enhance our understanding of how aging may affect weapons performance.

We are developing an ultrafast electron microscope and an ultrafast electron diffraction (UED) instrument to study complex transient phenomena, with the goal of achieving unprecedented combined spatial and temporal resolution (Figure 1). In the next two years, the prototype capabilities will combine in a single dynamic transmission electron microscope (DTEM). The DTEM instrument offers several unprecedented capabilities:

- Imaging time resolution of less than 1 nanosecond, with a goal of 10 picoseconds
- Interframe time of 5 nanoseconds or less
- Diffraction streaking time resolution of less than 10 picoseconds, with a goal of approximately 500 femtoseconds
- Imaging spatial resolution of less than 100 nanometers at less than 1 nanosecond time resolution, with a goal of 20 nanometers.

We have identified a number of other groups who have unique expertise in ultrafast methods to reveal transient structures and develop ultrafast diagnostics for electron imaging. These groups include Arizona State University,

Figure 1. We are developing a dynamic transmission electron microscope to study complex, transient events with unprecedented spatial and temporal resolutions.





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Figure 2. Short-pulse, high-intensity laser experiments using the electron time-of-flight spectrometer shown here will help explore the behavior of materials in regimes previously unattainable.

Lawrence Berkeley National Laboratory, University of California at Davis, University of Illinois at Urbana-Champaign and at Chicago, University of Michigan, and Florida State University.

State-of-the-Art Technologies

A central scientific objective of MSTD is to establish a world-leading scientific and experimentally validated set of capabilities for predicting the properties and performances of materials under extreme conditions—whether dynamic, environmental, or nanometer-length scale. In order to realize this objective, MSTD has developed strategic technologies in the following scientific areas:

- In advanced materials and characterization, we completed the synthesis of high-performance molybdenum-silicon multilayer coatings for extreme-ultraviolet lithography. Its breakthrough discovery has received the recognition of a prestigious 2003 R&D 100 Award.
- In support of the National Ignition Facility (NIF) project, we have carried out fundamental studies of laser-matter coupling and other optical materials research. When completed in 2008, the 192-beam NIF will be the world's most energetic laser, requiring unprecedented applications of novel optical materials.
- We have made significant advances in our understanding of dynamic response of materials, including isentropic and shock-driven systems. We continue to investigate shock melting and refreeze-on-release, as well as simulations of shock-ablation in metals and dislocation multiplication under plastic deformation.
- In support of the Yucca Mountain Project, long-term corrosion studies are enhancing our fundamental understanding of corrosion in order to develop extremely corrosion-resistant materials for nuclear waste repositories.
- We have developed novel systems to study functionalization of silicon membranes and small-aperture tubes for selective capture of bio-organisms. These systems may have widespread applications in the homeland-security area.

Future Goals

MSTD is developing a vigorous, integrated, and comprehensive program to investigate the properties and performance of materials subjected to extreme dynamic conditions of pressure, temperature, strain, and strain rates. A particular focus will be the design of extreme dynamic materials experiments and the development of advanced in situ, real-time diagnostics on high-energy-density experimental platforms. In pursuit of this goal, MSTD is also developing a state-of-the-art experimental program in the area of ultrafast, dynamic electron microscopy and diffraction to expand Livermore's capabilities in the materials science of strongly driven systems.

MSTD's new Nanoscale Synthesis and Characterization Laboratory (NSCL) will allow CMS scientists to link and integrate nanoscale science and technology programmatic requirements with materials synthesis, design, assembly, and prototyping. The role of the NSCL will be to lead research and development activities for next-generation target science applications in national security, inertial confinement fusion, and energy and environment.

BioSecurity and Nanosciences Laboratory

A center that conducts scientific research to protect the nation against biological threats and natural-disease outbreaks

The BioSecurity and Nanosciences Laboratory (BSNL) is a multidisciplinary, multiprogrammatic initiative among five major directorates at Livermore, including Chemistry and Materials Science (lead); the Biology and Biotechnology Research Program; Physics and Advanced Technologies; Energy and Environment; and Nonproliferation, Arms Control, and

International Security. BSNL's mission is to provide the Laboratory with biochemical and biomaterials expertise. The BSNL supports Laboratory missions in biosecurity, human health, and Department of Energy's Genomics:GTL (formerly Genomes to Life) program. Principal research areas include proteomic analysis, bioaerosol science, pathogen signatures, bio-organic synthesis, nanofabrication of device platforms, and cellular- and molecular-scale measurements.

Strategic Theme-Related Accomplishments in 2003

In alignment with the CMS research theme of *science in support of national objectives at the intersection of chemistry, materials science, and biology*, BSNL scientists conduct multidisciplinary

research that helps our nation counter biological weapons, understand the molecular machinery of the cell, and fight life-threatening diseases. Our research findings can be used to help the nation's homeland-security organizations counter bioterrorism and to improve both human health and environmental quality.

The science of pathomics seeks to identify and understand changes in protein and metabolite expression levels in response to disease. This knowledge provides an early warning system for the onset of disease epidemics resulting naturally or from terrorism. One of the major challenges for pathomics scientists is to develop the tools to quantitatively analyze complex protein mixtures, such as those found in blood (Figure 1). During 2003, BSNL scientists made significant progress in analyzing these mixtures and measuring protein expression levels using mass spectrometric methods.

BSNL scientists have applied sophisticated chemical and physical imaging tools (Figure 2) to address the challenges of bio-forensics, which would play an important role immediately after a terrorism-related biological incident, such as an anthrax or ricin attack. The BSNL group has successfully used the atomic force microscope to image the detailed structure of *Bacillus* spores and *Vaccinia* viruses at the level of protein complexes and systematically removed successive layers to reveal the architecture of these pathogens. The department also uses the nanoSIMS, a secondary-ion mass spectrometer with an ultra-small ion beam, to map the isotopic signatures of *Bacillus* spores.

Objects such as quantum-dots and nanowires are often thought of as basic elements of nanofabrication. However, inverse structures such as nanopores are also likely to play a critical role in nanoscale devices. In 2003, BSNL scientists demonstrated that they could make a wide variety of nanopores in



Figure 1. Using mass spectrometry, our researchers have determined the structure of chemical-warfare enzymes that attach to surfaces. Detectors based on this technology may one day rapidly identify proteins in a blood sample in a few minutes rather than hours or days.



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silicon substrates and then derivatize the walls of the pores to give them specific chemical functionality. Scientists are now exploring ways to apply the technology to detection of single pieces of DNA, measurement of ultra-low levels of arsenic in water, and dialysis of nitrate-contaminated water.

BSNL researchers in the field of nanophotonics had a number of significant achievements in the area of molecular and cellular measurements that will be important in our effort to expand our role in biomolecular materials research and in the Genomics:GTL program, whose goal is to build on the successes of the Human Genome Project and achieve a fundamental and systematic understanding of life. For example, our scientists in the field of nanophotonics have used the phenomenon of surface-enhanced Raman scattering to make

intracellular pH probes. Using a chemical compound with a Raman spectrum that is pH-dependent, the group coated the compound on gold nanoparticles to provide significant surface enhancement of the Raman signal. The gold nanoparticles were then injected into living cells and imaged with a confocal microscope.

We also collaborated with UCLA scientists to use confocal microscopy, combined with a unique microfluidic chip, to obtain the first true, single-molecule measurement of protein-folding dynamics. Finally, BSNL researchers used the atomic force microscope to measure the interaction potentials between protein molecules, investigate the molecular mechanisms of kidney stone formation, and produce nanoscale chemical patterns to template the attachment of virus particles at surfaces.

State-of-the-Art Technologies

BSNL has brought together a unique suite of analytical tools that provide advanced characterization capabilities at the molecular to single-organism level. Our investment in optical systems with single-molecule detection capabilities supports both ultrasensitive-detection development and research into protein-protein interactions. We have also acquired the most precise mass spectrometry systems available, which provide a technical basis for high-throughput protein analysis and profiling of chemical signatures across individual cells.

In addition, BSNL has created atomic force microscopy laboratories with the capability to spatially resolve a structure at the single-protein level, measure interaction forces at the single-molecule level, and chemically pattern surfaces at 10-nanometer length scales. These laboratories allow BSNL scientists to pursue a wide range of research activities focused on both biosecurity technologies and fundamental biosciences.

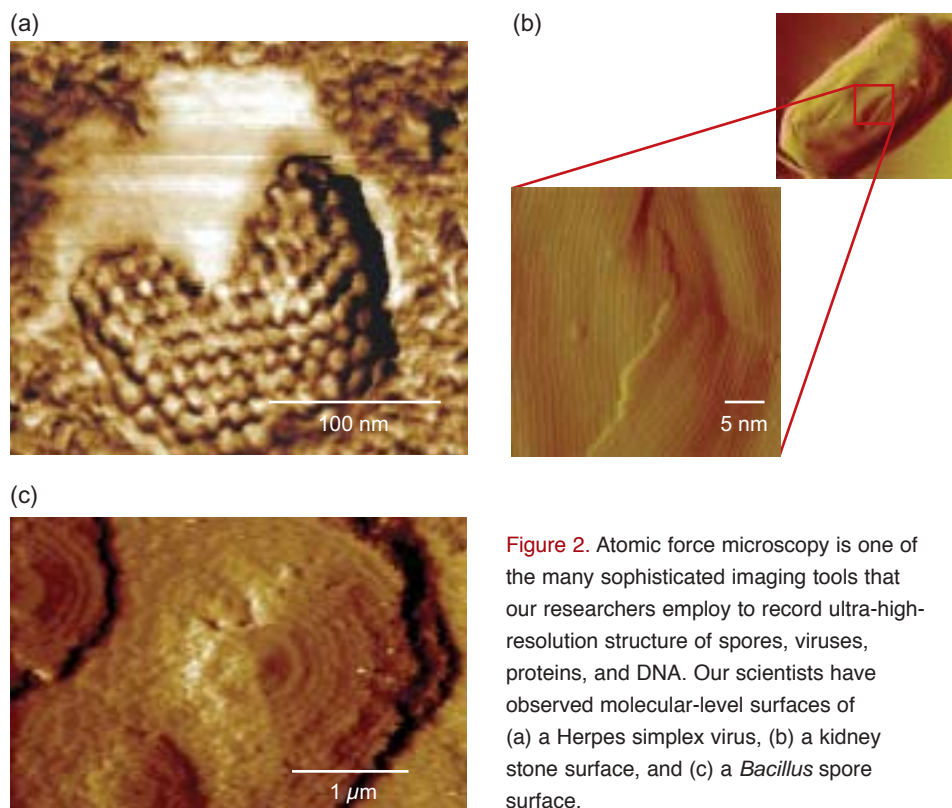


Figure 2. Atomic force microscopy is one of the many sophisticated imaging tools that our researchers employ to record ultra-high-resolution structure of spores, viruses, proteins, and DNA. Our scientists have observed molecular-level surfaces of (a) a Herpes simplex virus, (b) a kidney stone surface, and (c) a *Bacillus* spore surface.

Future Goals

In the coming year, we expect to make advancements in developing molecular-recognition chemistry using a variety of approaches, from combined methods for building self-selecting libraries of small-molecule ligands to the use of cells as in vivo chemical factories. The resulting recognition compounds will be central to all of our missions, whether through their ability to grab onto specific biological agents, their utility as site-specific tags and handles for studying protein dynamics, or their applications in targeted drug delivery.

Energetic Materials Center

A national resource for research and development of explosives, pyrotechnics, and propellants

L LNL's involvement in energetic materials began in 1952, when the Laboratory instituted a research and development program in high explosives for nuclear weapons. Today this work continues under the aegis of the Energetic Materials Center (EMC) as a core element of the Stockpile Stewardship Program at LLNL. In addition, the scope of work has broadened to support energetic materials research and development for advanced conventional weapons, rocket and gun propellants, homeland security, demilitarization, and industrial applications of energetic materials.

Underlying our activities in the EMC is a foundation of world-class science. The requirements of stockpile stewardship and the challenges for the development of advanced conventional weapons demand that we understand, with high fidelity, the performance of high explosives and how this may change over time. The evolving threats included in homeland security have expanded the scope of the required materials knowledge. Through the EMC, the Laboratory's scientists and engineers are coupling modern experimental tools with advanced theoretical and computational techniques to acquire detailed understanding of energetic materials that can be applied to the practical problems of national defense.

Strategic Theme-Related Accomplishments in 2003

A major accomplishment this year was our new capability to study the propagation of a detonation wave in complex geometries using flash radiography. This is particularly important for the insensitive high explosives commonly used in modern nuclear weapons.

We performed a series of experiments designed to produce a detonation front that turns a corner away from the direct influence of the initiating impulse. We have built a high-flux radiography system to monitor the shape of the detonation front in LX-17, an insensitive TATB-based explosive. Figure 1 illustrates the experiment assembly and the radiographs taken.

In the experiments, a detonator drives a detonation in the TATB hemispherical booster, which is designed to produce a uniform hemispherical shock into the LX-17 main charge. Because the detonator and booster are inset into the main charge, the detonation front in the main charge must turn away from the booster in order to propagate into the annular region of LX-17 that lies above the booster.

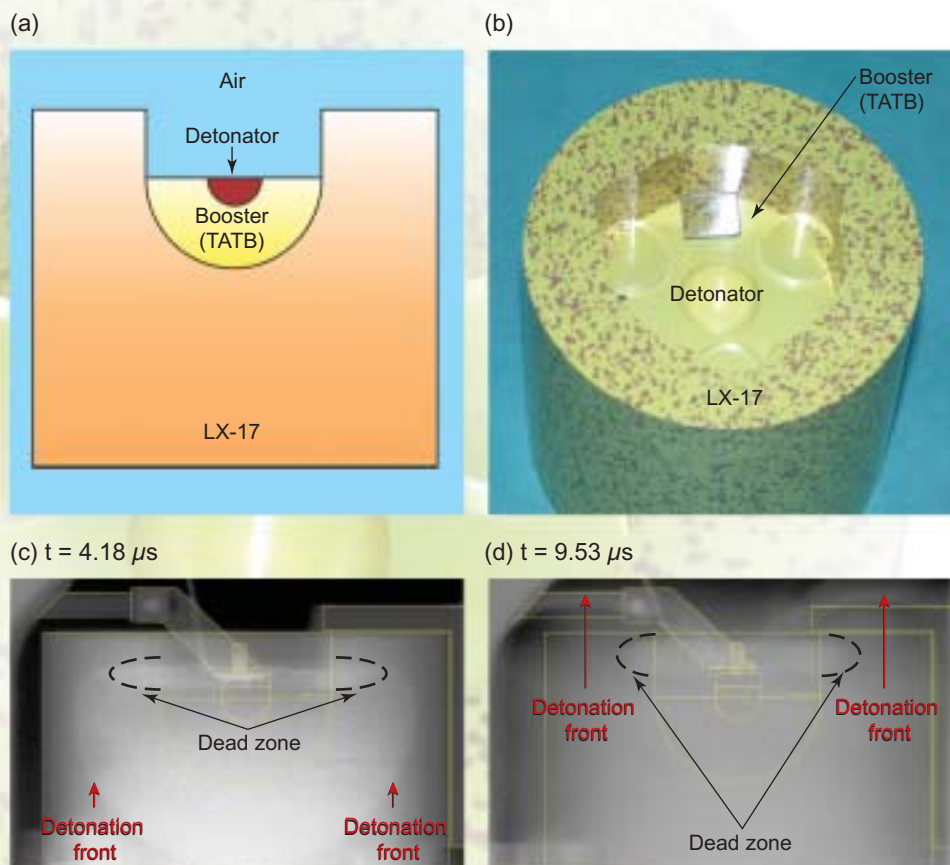


Figure 1. Using flash radiography, we have recorded, for the first time, a “dead zone” in the detonation propagation of high explosives, such as LX-17 and TATB. Because the detonator and booster are inset into the LX-17 main charge (a, b), the detonation front in the main charge must turn away from the booster in order to propagate into the annular region of LX-17 that lies above the booster.



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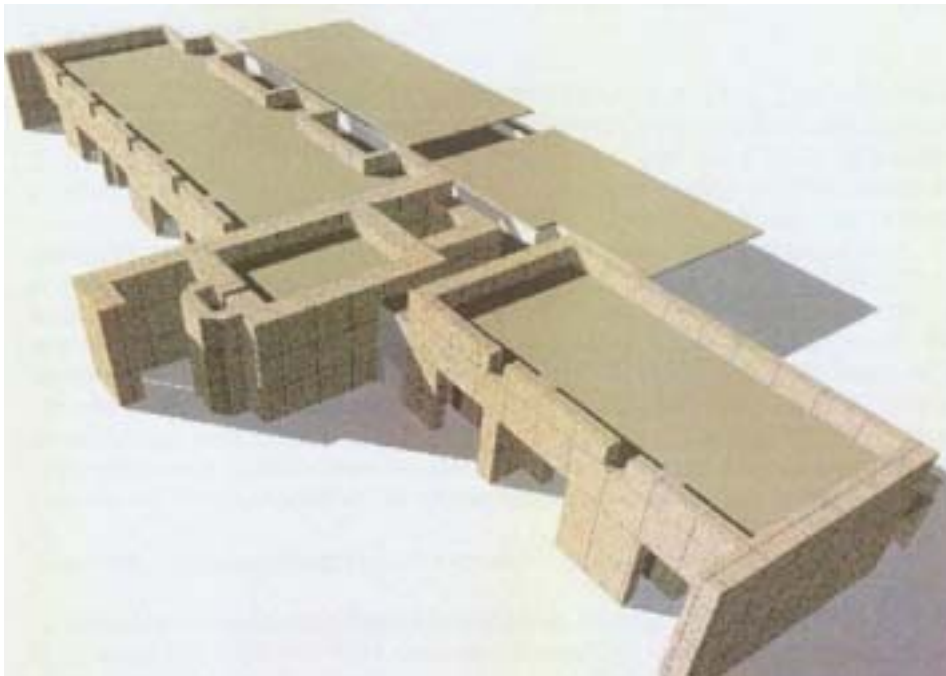


Figure 2. The new Energetic Materials Processing Center, a \$47M facility at Site 300, will offer a streamlined capability for the fabrication of explosive materials.

The radiographs taken from the experiment (Figure 1c and d) show a “dead zone” above the booster where there is no detonation. They also show that the “dead zone” has been compressed into an annular disk. The presence of this dead zone points out the need for improvement in current detonation models, since they do not predict its existence.

State-of-the-Art Technologies

To understand and control the chemistry of explosive reactions (nanosecond reactions driving microsecond detonation processes), state-of-the-art experimental facilities are required. The Laboratory’s unique explosive-testing facilities include the following:

- The High Explosives Application Facility (HEAF) and Site 300, in which explosives synthesis, formulation, characterization, processing, and testing are carried out.
- The Contained Firing Facility, and the Big Explosives Experimental Facility,

in which fully diagnosed explosives detonations are conducted.

- The Forensic Science Center, in which explosive detection methods are developed.

A major development this year was the design for the Energetic Materials Processing Center (Figure 2), a \$47M facility to replace aging CMS facilities at Site 300 with a streamlined capability for fabrication of explosives.

In our experimental facilities, we apply high-fidelity, high-speed diagnostics—including flash radiography, high-speed photography, laser velocimetry, and embedded particle velocity and pressure gauges—to dynamic experiments whenever possible. The coupling of experimental results with new computer codes and computational chemistry advances gives us a unique ability to apply the latest scientific developments to the challenges posed by energetic materials.

Future Goals

The combination of cutting-edge computational analysis and highly diagnosed experiments will provide advances in the area of energetic materials research. We are focusing on four major categories: performance, safety, reliability/surveillance, and new materials.

Our new diagnostic tools to observe the propagation of a detonation wave will enable the development of improved tools to analyze the performance of existing and new systems. It will also help develop more effective applications of insensitive explosives in the stockpile and in conventional weapons. Similarly, this approach will lead to the ability to evaluate the response of energetic materials to a wide variety of stimuli, providing a scientific basis for resolving safety questions and improving designs with respect to safety.

We also focus on detailed understanding of aging effects in energetic materials, with goals of identifying potential age-related changes and of extending the projected lifetime of energetic materials. Finally, we are developing novel energetic molecules, formulations, and nanoenergetics to support improved safety and performance in the stockpile as well as the trend toward small, high-value weapon systems that require innovative materials.

Forensic Science Center

Supporting national-security needs in chemical, nuclear, biological, and high-explosives counterterrorism with exceptional analytical capabilities

The Forensic Science Center (FSC) provides advanced analysis for Livermore's national-security programs in chemical, nuclear, and biological counterterrorism. While serving the immediate, short-term needs in these areas, the center also develops a technology portfolio to support long-term missions.

In addition, we are strongly engaged in international and national interests through a variety of federal agencies, including the Federal Bureau of Investigation (FBI), the Department of Homeland Security, and the Food and Drug Administration. The FSC receives, analyzes, and identifies unknown samples for all types of threats. We leverage this expertise in a number of ways to support established collaborations and provide scientific, technical, and programmatic planning leadership to emerging national and interagency efforts in the areas of

national security, nonproliferation, and intelligence support.

Strategic Theme-Related Accomplishments in 2003

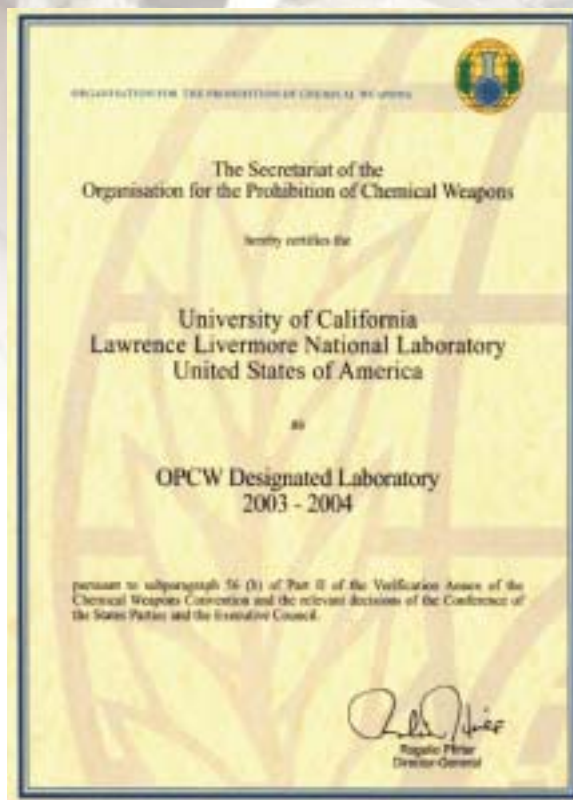
The work at FSC supports two CMS research themes: (1) *science in support of national objectives at the intersection of chemistry, materials science, and biology* and (2) *applied nuclear science for human health and national security*.

The FSC completed a three-year certification process to become the second U.S. facility qualified by the Organization for the Prohibition of Chemical Weapons (OPCW) to analyze samples that may contain chemical warfare agents (see separate article). Selected by the State Department in 2000 to seek OPCW certification, the FSC passed three grueling proficiency tests, demonstrating the center's advanced capabilities in detecting and analyzing small traces of unknown materials (Figure 1).

The FSC's interactions with federal agencies are growing steadily. In 2003, the FSC began working with the FBI to develop protocols for the decontamination of evidence that may contain radiological and nuclear materials. To aid law enforcement investigations, the FSC is leading the protocol development for DNA and trace evidence that is radiologically contaminated. In the areas of chemistry and explosives, the FSC also shares the protocol development with the Savannah River Technology Center.

We have developed a new chemical linking method that anchors selected functional molecules to silicon surfaces. Because of the heightened interest in sensor development for counterterrorism, porous silicon—with its photoluminescence properties—is an ideal sensor material for detecting chemical and biological agents. By covering the surface with biomolecules such as modified enzymes or antibodies, we can connect the receptor site to the porous silicon

Figure 1. The Organization for the Prohibition of Chemical Weapons (OPCW) in 2003 certified Livermore's Forensic Science Center as the second U.S. facility designated to support OPCW's chemical weapons inspection.





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Figure 2. Our scientists use a suite of analytical tools, such as a thermal desorption gas chromatograph—mass spectrometer shown here, to analyze unknown samples for potential chemical agents.

without destroying the photoluminescence. This new linking system is less synthetically laborious and less deleterious to the photoluminescence of the silicon.

State-of-the-Art Technologies

We are continually searching for new ways to combine analytical methods with challenging new applications, as well as packaging those tools into smaller, more compact, and more sensitive configurations to provide portability and flexibility in the field. These compact instruments provide mobile chemistry laboratories that greatly expedite data acquisition and decision making.

For example, we have developed a portable gas chromatograph–mass spectrometer (GC–MS), which has been deployed worldwide and is currently being manufactured under licenses to Constellation Technologies, Inc. and Kobelco Ltd., Japan. The Mini GC–MS is a robust, reliable, and field-deployable instrument. With an ability to analyze samples at sensitivities of parts per billion

within 15 to 40 minutes, the portable GC–MS can be used during homeland-defense activities, incident response, and law-enforcement investigations. This instrument, weighing only 60 pounds in a highly efficient configuration, will have potentially far-reaching impact on advancing the field of forensic science.

We have continued work on new materials for solid-phase microextraction in which a small, polymer-coated fiber resides inside a device similar to a syringe needle. The polymer acts as a sponge, soaking up organic compounds in seconds, without the need for additional solvents or other support. This also makes it possible to extract extremely small samples that can then be removed for subsequent analysis.

We have developed techniques for characterization of ultra-small fibers, particles, metal fragments, spores, and other materials with minimal sample preparation. This capability combines several established techniques, resulting in laser ablation–time-of-flight mass spectrometry.

Future Goals

The FSC is poised to be an integral component of the national response network for domestic events involving weapons of mass destruction and conventional terrorism. We continue to develop our increasing roles in significant arenas for national security. As the Department of Homeland Security develops, integrating Livermore forensic activities with other national assets, such as the National Biodefense Analysis and Countermeasures Center, will be critically important. The FSC is working with Livermore's Chemical, Biological, and Nonproliferation Program to establish bioforensics activities to support these goals.

FSC scientists will also continue to expand their basic science capabilities in the research areas of analytical science and instrument development, nuclear forensic analysis, and new molecular and nanostructured materials synthesis. These three scientific thrust areas effectively overlap our long-term programmatic needs and should position FSC to provide critical leadership for new programmatic areas in the future. Working with the Department of Homeland Security, the FBI, the Department of Energy, and pertinent intelligence agencies, FSC is strengthening programmatic connections that will use FSC and other unique resources in CMS and the rest of the Laboratory.

Glenn T. Seaborg Institute

Fostering research in fundamental and applied nuclear science and technology

The Glenn T. Seaborg Institute (GTSI) was established in 1991 to foster research in fundamental and applied nuclear science and technology. The nuclear and bionuclear science efforts at GTSI focus on:

- Science that advances the safety and reliability of the nation's nuclear-weapons stockpile
- Research to reveal new ways to counter terrorism and deter the proliferation of nuclear materials
- Applying radiation science to improve human health
- Scientific methodologies for assessing the vulnerability of the drinking-water supply and for characterizing the environmental impact of nuclear testing

- Science education to enhance public understanding and student involvement in nuclear research

These efforts contribute to the Laboratory's national-security missions, while promoting a clean environment and aiding the detection and treatment of disease. Our research enhances and anticipates the national-security efforts by ensuring a strong nuclear-science workforce and developing advanced detection techniques that use isotopic, radioactive, and biological signatures to identify and characterize the effects of radioactive and nuclear-proliferation materials.

Strategic Theme-Related Accomplishments for 2003

Research conducted by the GTSI aligns with the CMS research theme of *applied nuclear science for human health and national security*. The highlights of 2003 accomplishments include the following:

Our work has led to a new explanation for the surprisingly high cancer-response rates in patients treated with molecular-targeted radioisotope therapy for non-

Hodgkin's lymphoma. In this type of therapy, a monoclonal antibody (Lym-1)—known to preferentially target malignant lymphocytes—is attached to a radioisotope, ^{131}I in this case, resulting in a significant amount of radioisotope accumulation in the afflicted lymph nodes (Figure 1). Clinical trials have reported surprisingly high response rates to this therapy. In collaboration with clinical studies at the University of California at Davis, we have found that many lymph nodes shrink within a few days after receiving the monoclonal antibody-radioisotope dose. The dose results in an increased concentration of radioactive source within the lymph node, which increases the efficiency of the targeted radioisotope therapy.

A second project involving a related aspect of radioisotope therapy has led to new ways to reduce the liver damage from cancer treatment. Radioimmunotherapy is a method in which large molecules incorporating both a radioisotope and a monoclonal antibody are injected and bind to targets such as breast cancer or lymphoma tissue. The β decay of the radioisotope lodged in the tumor then destroys some of the cancerous material. Because not all of the radiotherapy material actually arrives at the intended site and eventually must be treated by the liver, we have designed a biodegradable segment in these large molecules so that the large molecule will fall into smaller pieces, making it easier for the liver to process and avoid damage from the radioactivity.

This work also compared the use of three radioisotopes in this type of therapy, finding that in some important cases, ^{90}Y was preferable to the more commonly used ^{131}I because the β decay was more energetic and the targeting more specific for ^{90}Y . A third radioisotope, ^{111}In , was very useful for imaging the deposition of the radioisotopes because, instead of β decay, the ^{111}In produces a γ ray, which





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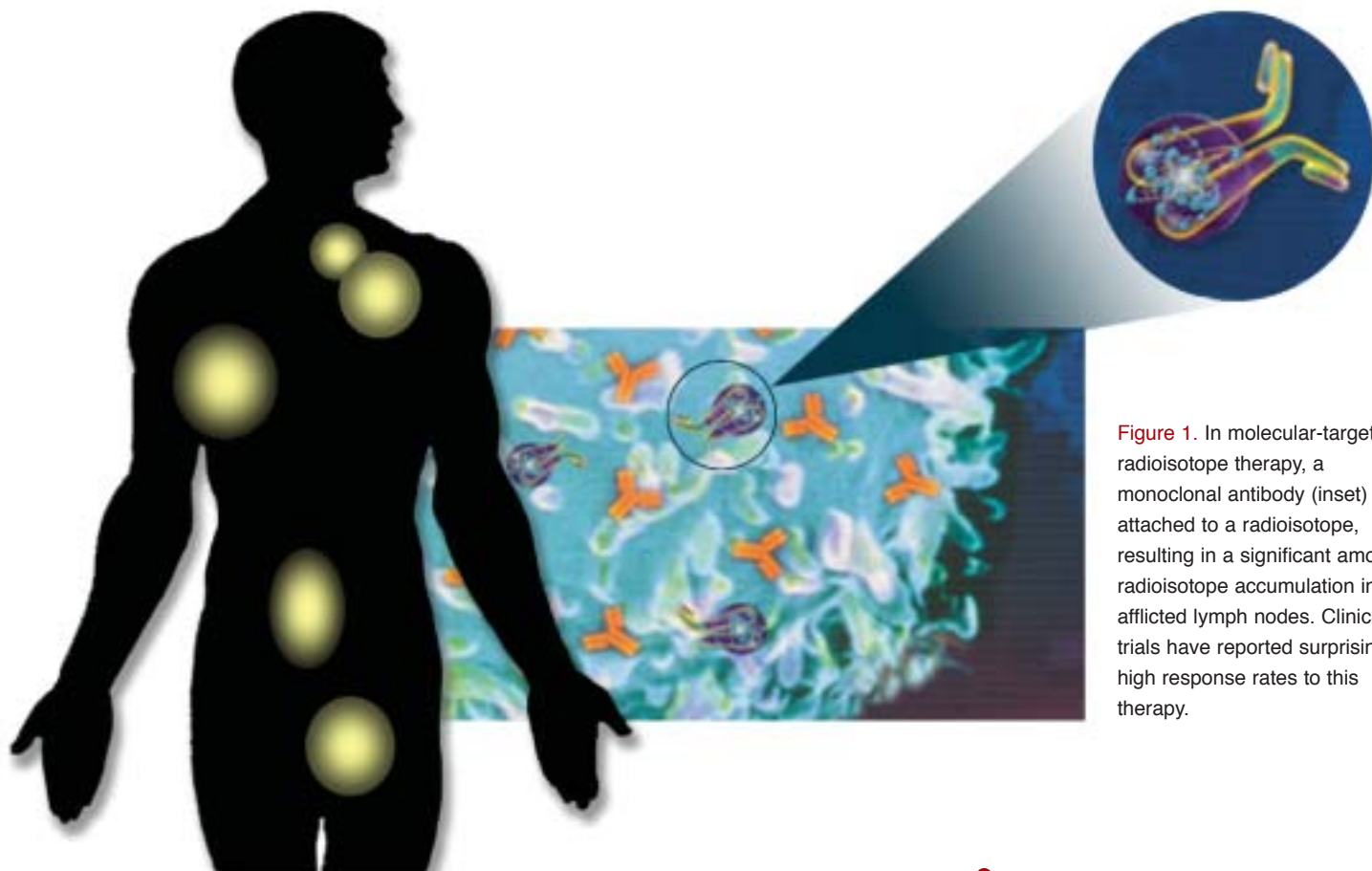


Figure 1. In molecular-targeted radioisotope therapy, a monoclonal antibody (inset) is attached to a radioisotope, resulting in a significant amount of radioisotope accumulation in the afflicted lymph nodes. Clinical trials have reported surprisingly high response rates to this therapy.

can be used to trace the location of the radioisotope.

Under the umbrella of GTSI, our scientists have added the discovery of elements 113 and 115 to Livermore's previous discoveries of elements 114 and 116. Details of this work are covered under a separate article in this report.

State-of-the-Art Technologies

The institute initiated three new projects during the past year. The first effort is to develop synthetic, high-affinity ligands (SHALs) that are targeted against non-Hodgkin's lymphoma. The second project will determine the feasibility of using gene expression to estimate the radiation dose in people, with pilot studies on person-to-person variability and time-dependence of the gene-expression signal. The third project initiated an effort to use radiation-induced gene expression for

post-exposure dosimetry to improve the accuracy of victim triage following a nuclear or radiological event.

We also began detector development for the Majorana project to measure the mass of the neutrino and will determine whether hadrons (for example, protons and neutrons) and leptons (for example, neutrinos and electrons) are conserved separately, as assumed now, or should be combined in a unified model.

GTSI's Nuclear Science Internship Program, sponsored by the Department of Energy, provides nuclear science students with individual mentors who train students in nuclear and analytical chemistry methods. During the summer of 2003, GTSI hosted 20 college graduate and undergraduate students. Leveraging our scientific leadership in age-dating groundwater, we are collaborating with University of Arizona to study the source, transport, and fate of nitrate—a common contaminant—in groundwater.

Future Goals

Our goals are to enhance the impact of nuclear and bionuclear science on important national problems such as homeland security, health, and the environment. Together with national security organizations, we will apply the science of isotopic signatures to identify illicit manufacturers of biological and nuclear weapons. We will also apply nuclear and bionuclear science to minimize the effects of nuclear and radiological weapons. In addition, we will continue our quest to study nature's newest elements as well as our efforts to improve the accuracy and effectiveness of molecular-targeted radioisotope therapy for advanced cancer.

Center for National Security Applications of Magnetic Resonance

Probing the structure and dynamics of molecules and materials for science in the national interest

In 2003, CMS and the Biology and Biotechnology Research Program (BBRP) at LLNL jointly established the Center for National Security Applications of Magnetic Resonance. The center houses a multidisciplinary, state-of-the-art, nuclear magnetic resonance (NMR) facility dedicated to exploratory research and Laboratory mission-related challenges in biological characterization and national defense (Figure 1). NMR uses large magnetic fields and radio frequency spectroscopy to probe the structure and dynamics of molecules and materials and enable the study of large

biomolecules in physiologically relevant solution conditions. NMR can also provide dynamic insight into the structural changes that occur as a protein folds and unfolds while carrying out its function.

The center provides Livermore programs with a powerful resource for the elucidation of chemical, physical, structural, dynamic, and mechanical properties in a broad range of biological, organic, and inorganic materials. Of special interest is the structure of high-molecular-weight organic and inorganic polymers, proteins, RNA (ribonucleic acid), membrane proteins, and DNA-protein complexes.

The unique collocation of facilities and expertise at the center will be valuable especially to weapons research, such as materials aging study and national-security efforts. The integration of structural biology with materials characterization using NMR expertise will provide a complementary resource of skills and knowledge that serves

as a model for beneficial consolidation of facilities and scientists.

Strategic Theme-Related Accomplishments for 2003

One of the central concerns of the U.S. Stockpile Stewardship Program is the aging of weapons components over lengths of time much longer than the weapon was expected to remain in service. For example, among the most relevant processes that may affect the lifetime of polymer materials used in weapons are interactions with radiation and the effects of desiccating environments.

NMR is a valuable technique that complements solvent-swelling methods and dynamic mechanical analysis (DMA) to unravel the molecular level origins of material degradation. In particular, it is difficult to measure mechanical property changes due to desiccation using DMA and solvent-swelling methods, because removal of material from the desiccating environment rapidly rehydrates the material—returning the material to its unperturbed state. NMR, however, evaluates these values in situ by analyzing changes in chain dynamics which depend directly on crosslink density and strongly influence changes in material properties, without requiring the material to be removed.

In addition, we are extending NMR techniques to much smaller spatial scales to improve the spatial resolution and sensitivity of the technique. The ultimate sensitivity of NMR is related to the dimensions of the radio frequency coil that generates and detects NMR signals. By decreasing coil size, we have demonstrated significant improvements in NMR sensitivity. In addition, in imaging applications, the spatial resolution obtainable is dependent on the sensitivity of the NMR hardware. Thus, higher sensitivity coils allow for the magnetic



Figure 1. Spectrometers housed in the new Center for National Security Applications of Magnetic Resonance will contribute to chemical, molecular, and materials studies important to nonproliferation, biotechnology, and stockpile stewardship programs.



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Figure 2. Magnetic resonance image of a micro-catheter submerged in fluid. Flow and diffusion-weighted imaging are being used to investigate turbulence contributions to tissue-fluid interactions near catheter implants.

resonance-based imaging with increasing spatial resolution (Figure 2). During 2003, we used lithography to produce coils with outer diameters of 360 micrometers, which is more than 15 times smaller than standard coils and provide an improvement in mass sensitivity by a factor of 350. This research and development is at the cutting edge of NMR technology, and it will result in the development and deployment of new laboratory and field-based NMR instruments for identification, attribution, and treaty verification investigations, particularly for chemical agent signatures.

State-of-the-Art Technologies

We are using NMR to determine the binding activity of small molecules to Clostridial neurotoxins and anthrax proteins in order to develop synthetic, high-affinity ligands (SHALs) for use as antidotes and/or detection reagents. Similar studies are being carried out on HLA-DR10, which is a non-Hodgkin's lymphoma cell receptor, in order to develop SHALs for radioimmunotherapy.

Livermore scientists are also using NMR methods to understand how adduct

conformation affects cellular responses to DNA damage. Covalent binding of bulky ligands to DNA can alter biological processing of the DNA by cellular proteins governing replication, transcription, and repair, causing mutations and ultimately cancer, especially if the lesion is located in an oncogene or a tumor-suppressor gene. We have determined a novel structure of a DNA adduct (O6-[4-oxo-4-(3-pyridyl)butyl]guanine in an 11-mer duplex) derived from a tobacco-specific carcinogen. The structural insights derived from our NMR study can be used to understand the carcinogenesis and to derive therapeutic strategies for such carcinogens.

We have also collaborated with Sandia National Laboratory and the National Renewable Energy Laboratory to characterize new hydrogen storage materials by advanced solid-state NMR methods. Safe and compact storage of hydrogen—a clean alternative to fossil fuel—is an important research area, and the NMR techniques are making strong contributions toward a better understanding of its storage requirements.

Future Goals

In collaboration with Livermore's Center for Accelerator Mass Spectrometry, we are using solid-state NMR methods to understand the role of soils and dissolved organic carbon in the carbon cycle and in carbon sequestration. NMR is providing key data for a better mechanistic understanding of the formation, transport, and transformation of organic carbon. These results will be used to enhance the quality of ocean-climate-carbon models used to predict future carbon cycle changes. In addition, we are employing magnetic resonance imaging methods to generate three dimensional maps of modulus changes in aged and stressed materials, implant interactions with bio-tissue hosts, and sub-millimeter assemblies of materials that make up experimental targets for high-energy-density physics.

Postdoctoral Fellows and Graduate Students

The Postdoctoral Program at CMS continues to draw high-caliber young scientists to the Laboratory. They came from top universities across the world, bringing fresh ideas and leading-edge skills to our community. Many of our postdoctoral fellows are making significant contributions to key Laboratory programs; others maintain a close tie to external collaborators. Approximately 40 postdoctoral researchers serve in CMS in a wide range of disciplines. There are also about 15 graduate students pursuing doctorate degrees within the directorate, each under the supervision of a CMS scientist and a faculty thesis advisor. The following is a list of their research interests grouped according to our current strategic areas.

Nuclear Magnetic Resonance

Three postdoctoral researchers form the core staff for the new Center for National Security Applications of Magnetic Resonance. **Sarah Chinn** (UC Davis) is studying polymer aging, carbon sequestration in soil and ocean sediments, and aerogel formation. **Julie Herberg** (Washington University) analyzes bacterial spores and hydrogen storage in nanoporous materials. **Anh-Tuyet Tran** (UC Davis) is working on biological applications of nuclear magnetic resonance, and graduate student **Anant Paravastu** (UC Berkeley) is studying optical pumping of semiconductors.

Nanoscale Materials Science and Technology

Many of the postdoctoral researchers and graduate students in this discipline area are associated with the new Nanoscale Synthesis and Characterization Laboratory. **Wonyoung Choe** (Iowa State) continues his work on magnetic nanoparticles involving cleaving and

reforming covalent bonds between silicon and germanium. **Rob Meulenberg** (UC Santa Barbara) works on properties of cadmium–selenium quantum dots, measuring the optical and electronic properties of semiconductor materials. **Raluca Negres** (Central Florida) is developing conditioning protocols for nonlinear crystals. **Yinmin “Morris” Wang** (Johns Hopkins) is studying the applicability of nanocrystalline synthesis and characterization techniques for fabrication of high-energy-density experimental targets, and Lawrence Fellow **Sergei Kucheyev** (Australian National University) has been studying defects created in optical materials by irradiation with particle and laser beams.

Graduate student **Trevor Willey** (UC Davis) is characterizing self-assembling monolayers and surface-attached interlocking molecules using synchrotron radiation. **Joakim Nilsson** (Stockholm University) is pursuing the area of nanomaterials and nanotechnology.

Nuclear Materials Stewardship

Bassem El-Dasher (Carnegie–Mellon University) and **Jeremy Gray** (U.C. Davis) are studying damage and stress of bulk polycrystalline and nanocrystalline materials, together with properties and evolution of colloidal particles, as they are related to the Yucca Mountain Project.

Correlated Electron Systems and Alloy Properties

Tom Trelenberg (Florida State) and **Stephen Glade** (California Institute of Technology) carried out a study of the synthesis and characterization of nanoparticles and very thin films of plutonium and other actinides, using a wide range of spectroscopic techniques. **Kerri Blobaum** (Johns Hopkins) is investigating phase transformations and phase stability in plutonium–gallium alloys. **David Clatterbuck** (UC Berkeley) has been

measuring the phonon dispersion curves and studying the phase transformation behavior of plutonium using synchrotron radiation-based methods.

Dynamic Properties of Materials

Bryan Reed (Cornell) is heavily involved in the development of ultra-fast electron microscopes for studying material and molecular processes on the nanometer and picosecond scales. **Andrew Ziegler** (UC Berkeley) is conducting critical experiments addressing unsolved problems of theoretical crystal plasticity models, the development of a new ultrafast transmission electron microscope, phase transformations, and rapid melting and resolidification processes. **Jonathan Crowhurst** (University of the Witwatersrand, South Africa) is using impulsive stimulated light scattering to measure elastic constants and other properties at extremely high pressures. He is also studying the physical and chemical behavior of water and other materials under simultaneous conditions of high pressure and temperature. Graduate student **Monica Barney** (UC Davis) is pursuing a thesis in the area of dynamic properties of metals, including the effects of thermal cycling and aging.

High-Performance Computing

Lawrence Fellow **Wei Cai** (MIT) has made important contributions to the science of dislocations (see separate article) and is about to assume a faculty position at Stanford University. **Will Kuo** (UC Irvine) has studied the structure of bulk water and the nature of the water–air interface (see separate article), and he is applying the same tools to study DNA properties. **Bahrad Sokhansanj** (UC Davis) is analyzing spontaneous and environmentally caused DNA damage and repair, and **Aaron Golumbskie** (UC Berkeley) is simulating intercellular



signaling pathways in epithelial cell tissue with a view toward understanding the mechanism by which cystic fibrosis leads to disease. **Brad Pesavento** (Baylor College of Medicine) has been working to help elucidate pathogen signatures and detect infections before symptoms are noticed.

Nir Goldman (UC Berkeley) is using first-principles quantum mechanical computational chemistry to study liquids at extreme pressures and temperatures.

Luis Zepeda-Ruiz (UC Santa Barbara) is using kinetic Monte Carlo techniques to study crystal growth that will impact high-power-laser optics, high-explosives materials, and biomineralization experiments. Graduate student **Lilian Davila** (UC Davis) is studying damage in fused silica from radiation.

Biophysical and Interfacial Science

Many postdoctoral members in this group are part of the BioSecurity and Nanosciences Laboratory. Lawrence Fellow **Julio Camarero** (University of Barcelona) is working on a variety of projects in bio-organic synthesis and protein chemistry. **Barry Cheung** (Harvard) is working on the assembly of 2D protein and virus arrays on nanometric chemical templates. **Marco Plomp** (University of Nijmegen, The

Netherlands) is using atomic force microscopy to study the ultrastructure of pathogens such as viruses and bacterial spores. **Tim Ratto** (UC Davis) is building a capability to perform molecular recognition force spectroscopy to conduct measurements on quantities such as adhesion properties of materials in high-energy-density experimental targets or biological applications such as protein-ligand interactions on cell surfaces. **David Hertzog** (Stanford) is studying microfluidics and macromolecular dynamics in mixing for protein folding. **Jason Holt** (California Institute of Technology) is studying carbon nanotube-based permeable membranes for separations, chemical and biosensing, and the fundamentals of nanoscale fluid mechanics. **Roger Qiu** (UC Riverside) is revealing the molecular modulation of kidney stone formation by naturally occurring small molecules and proteins.

Graduate student **Julie Muyco** (UC San Diego) is studying the interaction between titanium in orthopedic and dental implants with hydrogen peroxide, a reactive chemical produced in the body during inflammation. **Alex Artyukhin** (UC Davis) is working on a thesis to develop a carbon nanotube-based biosensor for bacterial toxin detection.

Other Programs

Brady Clapsaddle (Colorado State) has used sol-gel chemistry to develop highly dispersed inorganic or organic hybrid nanocomposites for applications such as gas-generating advanced energetic materials. **Erik Nelson** (Stanford) is using extended x-ray absorption fine-structure spectroscopy to investigate the local atomic environment and vibrational properties of plutonium and gallium in a mixed-phase alloy. **Joshua Patin** (UC Berkeley) is part of a group who has discovered new elements 113 and 115 (see separate article). **Julie Smith** (University of Western Australia) is studying chemical signatures in biological weapons, early earth geochemistry, and the isotopic composition of materials.

Lucile Dauffy (Texas A&M) works on the detection of radioactive materials placed inside cargo containers, Monte Carlo simulations for monitoring of highly enriched uranium, and medical dosimetry. **Tony Esposito** (University of Washington) is developing spectroscopic methods for ultrasensitive detection of chemical and biological samples. He is also characterizing the optical performance of high-refractive-index glass spheres for remote chemical and radiation sensing applications.

Awards and Recognition in 2003

R&D 100 Awards

Each year, R&D Magazine recognizes the 100 most technologically significant products of the year. CMS scientists played significant roles in two of the R&D 100 Awards for 2003

Extreme Ultraviolet Lithography Full-Field Step-and-Scan System

For decades, integrated circuits have steadily gotten faster, smaller, and cheaper. Circuit performance has approximately doubled every two years—a pace of development commonly referred to as Moore's Law. Fundamental physics laws on the diffraction of light are threatening this rate of development as the spatial definition of circuits on chips becomes limited by the wavelength of the light used to print those circuits. To print 100-nanometer features—the current size for computer chips—manufacturers have had to add expensive enhancements to lithographic systems. The enhanced systems use light in the deep ultraviolet part of the spectrum with wavelengths of 193 to 248 nanometers.

A multilaboratory research and development program, including Lawrence Livermore, Sandia, and Lawrence Berkeley national laboratories, has been working on developing a system for extreme ultraviolet lithography (EUVL), to print circuits with features smaller than before. The EUVL full-field step-and-scan system goes beyond deep ultraviolet into the EUV part of the spectrum, using light with wavelengths of about 13 nanometers—more than a factor of 10 shorter than the wavelength of even the most aggressive deep

ultraviolet system. The current resolution for the EUVL system is 50 nanometers, but the team projects that a resolution of 20 nanometers will ultimately be possible.

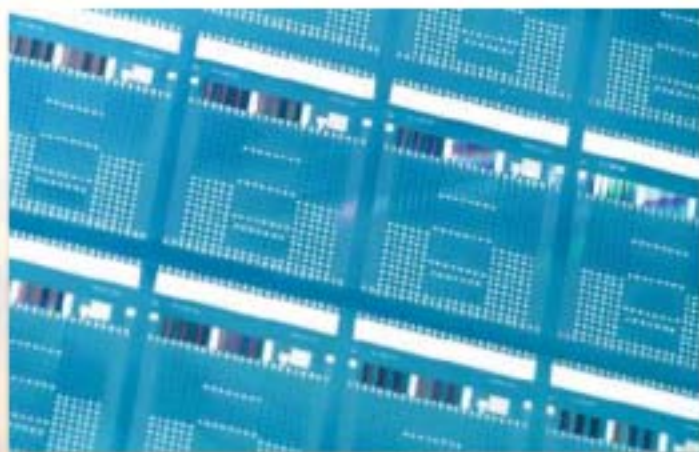
The EUVL system's development was key in convincing the microelectronics industry that EUV systems could follow deep ultraviolet systems as the next-generation lithography technology for producing microelectronics.

In addition to its application in the semiconductor manufacturing industry, the EUVL full-field step-and-scan system also has potential applications in nanotechnologies using photonic crystals, surface-acoustic-wave detectors, and molecular electronic devices that could benefit from the large surface area that can be imaged with features smaller than 50 nanometers.



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Front view of the extreme ultraviolet lithography full-field step-and-scan system (left). A close-up of the 24- by 32-millimeter fields that this technology can print on a silicon wafer (right).



Ion-Beam Thin-Film Planarization for Extreme Ultraviolet Lithography

As integration capability required for computer chips increases, conventional optical lithography—the current practice of directing light through a mask, or reticle, to print integrated circuits on chips, has been stretched to its limit. When beams of light cannot be made thinner, the number of circuits that can be written on a given chip can go no higher.

Extreme ultraviolet lithography (EUVL), which has emerged as the lithographic method of the future, is expected to be capable of reducing the feature size from 130 nanometers to less than 50 nanometers.

Paul Mirkarimi of CMS led the team that received an R&D 100 Award in 2003 for developing the technology to produce nearly perfectly smooth surfaces for reticles and other critical components for EUVL, even when the silicon substrate surfaces have serious defects. The team's ion-beam thin-film planarization process can smooth surfaces with particles piled up to 70 nanometers high.

A EUVL reticle blank consists of a substrate coated with a molybdenum-silicon multilayer film designed to have optimal reflectivity at extreme ultraviolet (EUV) wavelengths of 13 to 14 nanometers. Reflectivity is critical because EUVL uses strongly attenuated EUV light directed at reflective optical components to create minute features. The film is coated with a buffer layer and an absorber layer and is processed with an electron-beam lithographic tool to form a patterned EUVL reticle. The finished reticle absorbs EUV light at specific locations and reflects it everywhere else.

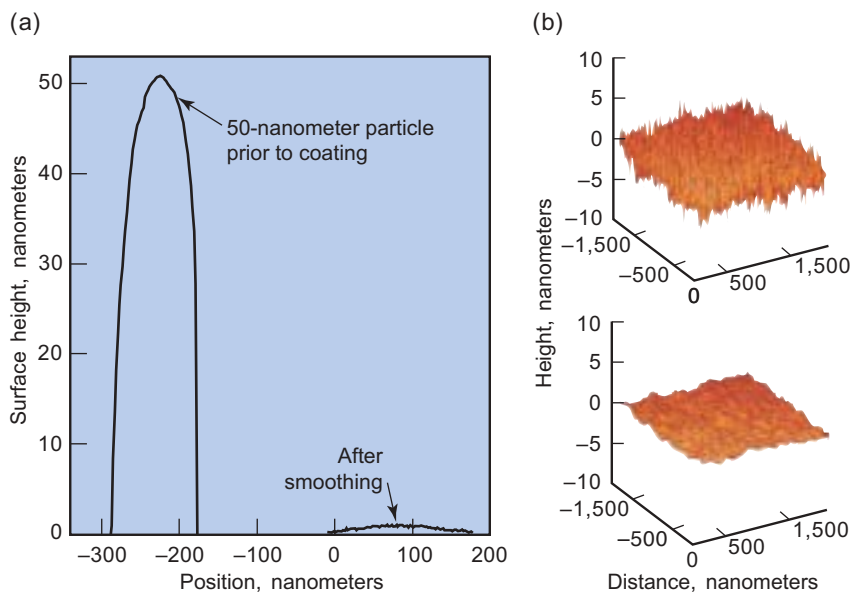
The ion-beam thin-film planarization process smoothes, or “planarizes,” substrate particles during the multilayer

coating process. A primary ion source sputters material off a target onto the substrate, and a second ion beam etches, assisting in the formation of a smooth, uniform film with remaining defects less than 1 nanometer high.

EUVL provides a smaller feature size that will allow more transistors to be placed on an integrated circuit. Applications will be widespread in the semiconductor industry. Desktop computer microprocessor chips, for example, will operate at more than 10 gigahertz, and random access memory chips can have gigabyte capacities, which will make a variety of computationally intensive applications practical.



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ion-beam thin-film planarization can be used to fabricate nearly defect-free reticles and projection optics for extreme ultraviolet lithography. (a) After the deposition and etching process, a 50-nanometer particle on the original wafer surface leaves almost no visible trace on the final surface. (b) Overall surface roughness is dramatically reduced as well by this process.



Jack Campbell



David Eaglesham



John Elmer



T.G. Nieh



Patrice Turchi

Krishnan
Balasubramanian

Professional Society Honors

• The American Ceramics Society gave the George W. Morey Award to CMS senior scientist **Jack Campbell**, the group leader for Advanced Optical Materials at the National Ignition Facility. Jack was honored for his “work and leadership in the development, characterization, and manufacturability of phosphate laser glass for high-peak power lasers.”

• **David Eaglesham**, the CMS chief technologist, was elected vice president (president-elect) of the Materials Research Society, the world’s leading forum for advanced, cutting-edge interdisciplinary materials research.

• **John Elmer**, the group leader for Materials Joining, was named a 2003 fellow of the American Society for Metals in recognition of his contributions to the use of synchrotron radiation in welding science. John’s award cited his “development and application of synchrotron-based, in situ, spatially resolved x-ray diffraction techniques to permit quantitative understanding of phase transformation kinetics during fusion welding.” He is also a recipient of the 2003 Warren F. Savage Memorial Award from the American Welding Society, for “innovative research resulting in a better understanding of the metallurgical principals related to welding.”

• **Christian Mailhot**, the division leader of the Materials Science and Technology Division, was elected a fellow of the American Physical Society (APS), an honor given to no more than 0.5% of the APS membership. Christian

was nominated by APS’s Division of Materials Physics for his “outstanding contributions and scientific leadership in theoretical and computational condensed matter and materials physics, with particular emphasis on innovative discoveries related to quantum-confined semiconductor structures and high-pressure research.”

• CMS metallurgist **T.G. Nieh** was named a 2004 fellow of The Minerals, Metals & Materials Society (TMS) for his “contributions to the understanding of the superplasticity behavior of metals and ceramics, including high strain rate superplasticity and superplastic ceramics.” No more than 100 of the nearly 10,000 TMS members can be living fellows.

• **Charlie Westbrook**, the CMS acting chief scientist, was elected vice president (president-elect) of the Combustion Institute, an international, scientific society that promotes and disseminates research in combustion science.

• The Materials Information Society, ASM International, has selected **Patrice Turchi**, a CMS physicist, to serve on the Alloy Phase Diagram Committee. The charter of ASM is to develop and improve publications and services that benefit the worldwide materials community.

• Organized by the World Association of Theoretically Oriented Chemists, the Robert S. Mulliken Lecture Series each year invites outstanding scientists to deliver a lecture at the Center for Computational Quantum Chemistry, University of Georgia. For 2003, Krishnan Balasubramanian was chosen for this distinguished honor.

• The American Chemical Society has elected **Bryan Balazs**, a CMS group leader, to its Committee on Education for 2004–2006 and as Chair of Subcommittee A (K–12). The ACS Society Committee on Education ensures that the ACS educational activities focus on critical chemical education issues across all levels of instruction.

Scientific Achievements

• A team of scientists from the CMS and Energy and Environment (E&E) directorates has been awarded the Laboratory’s Science and Technology Award by **Michael Anastasio**, director of the Laboratory. This award is the highest honor granted by the Laboratory for science and technology accomplishments. **Joe Wong**, **Adam Schwartz**, and **Mark Wall** of CMS and **Dan Farber**, **Florent Occelli**, and **Carl Boro** of E&E received this award for their work measuring the phonon dispersion curves of δ -plutonium–gallium. The team’s efforts represent an outstanding example of world-class fundamental science inspired by the mission-driven priorities of the Laboratory and of effective collaboration among a broad group of researchers.

• **Steve Letts** is the recipient of the Larry Foreman Award at the 15th Target Fabrication Specialists Meeting for sustained contributions to target fabrication science.

• **Raymond Friddle**, a graduate student working in the BioSecurity and Nanosciences Laboratory, won the best scientific poster prize at the 2003 Nanoscience and Bionanoscience

Research Meeting. Raymond's poster, "DNA compaction by yeast mitochondrial packing protein ABF2p," was coauthored by **R. Baskin** and **A. Noy**.

Leadership Positions

• CMS senior scientist **Joe Farmer** was selected as a member of the Defense Science Board (DSB) Task Force on Corrosion Control. The DSB's technical experts advise the Secretary of Defense on matters of interest to the Department of Defense.

Editorships

Many CMS scientists play important roles in their respective professional societies, with about 22 CMS researchers serving as editors or on the editorial boards of technical journals. These scientists provide a valuable connection between CMS and researchers at universities, other national laboratories, and important industries.

Patents and Licenses

CMS scientists and engineers participated in groundbreaking research that resulted in the following patents in 2003:

Invention Disclosures	23
Patent Applications	12
Patent Issued	7
Licenses Executed	3

Postdoctoral Fellows and Interns

• The Minerals, Metal & Materials Society (TMS) has awarded **Andrea Hodge**, a CMS postdoctoral student, the TMS Young Leader Internship Award. Given annually by the Structural Materials Division of the TMS, the Young Leader Award recognizes leadership potential in young scientists and provides an honorarium as well as travel and lodging for the TMS annual meetings. Andrea's current research focuses on developing nanostructured metal foams for high-energy-density experimental targets.

• **Sarah Nelson**, a graduate student participating in this year's Nuclear Science Internship Program, is the recipient of the 2003 American Institute of Chemists Award. This award is given each year to the most outstanding graduating senior in chemistry, biochemistry, and chemical engineering at UC Santa Barbara (UCSB).

Other Recognition

• CMS 2002 Annual Report receives an Award of Excellence from the Society of Technical Communications. In addition to highlights and accomplishments by more than 30 authors, a team of production staff—including **Theresa Healy**, **Dabbie Bowron**, **Emmeline Chen**, **Missy Davidson**, and **Scott Dougherty**—contributed to the high-quality debut of the annual report.

University Collaborations

The research activities of CMS members frequently include technical interactions with leading groups and individuals at universities in the United States and other countries. A few interactions with university research programs have been identified as particularly desirable and valuable, leading CMS to provide funding to these programs to facilitate interactions (for example by granting graduate students and faculty special access to the Laboratory). There were several such active collaborations in 2003:

- Dr. Brian Wirth of UC Berkeley partnered with **Christian Mailhot** to investigate material degradation and deformation.
- Dr. Chris Schuh of MIT partnered with **Mukul Kumar** on the higher order correlation data.
- Dr. Mildred Dresselhaus of MIT partnered with **Joe Satcher** to study carbon aerogels.
- Dr. Steven Quake of California Institute of Technology partnered with **David Eaglesham** on microfluidics technology.
- Dr. Dudley Herschbach of Harvard University partnered with **Carl Melius** to study extreme chemistry at high temperatures and pressures.
- Dr. Roberto Car of Princeton University partnered with **Lou Terminello** to investigate methods in computational materials science.



Bryan Balazs



Adam Schwartz



Mark Wall



Steve Letts



Joe Farmer



Andrea Hodge

In Memoriam

Maria Bartelt

Maria Bartelt, physicist and scientific capability leader for computational materials science in CMS, passed away at the age of 41 on June 23, 2003, due to complications from an opportunistic infection. Maria had been battling non-Hodgkins lymphoma for more than a year.

Maria joined Lawrence Livermore in 2000. Her work focused on dislocation dynamics and the growth of molecular crystals under near-equilibrium conditions from solutions. Most recently, she was working on a kinetic Monte Carlo approach to predicting computationally the templated nucleation and growth of macromolecular structures formed at nanoscale chemical patterns on surfaces.

Maria started her career as a research assistant at the Universidade de Aveiro in Portugal, where she received her diploma in theoretical, solid-state physics in 1984 for her work on amorphous systems. She received her master's degree in physics in 1989 and her Ph.D. in physics in 1991 from Clarkson University under Vladimir Privman. Maria was awarded the Graduate Student Distinction Prize and membership in the $\Phi\chi\Phi$ Honor Society for her work on surface and size effects in statistical mechanics, particularly irreversible adsorption, polymers, and interfaces.

After receiving her Ph.D., Maria became a postdoctoral research associate at Iowa State University in Ames, Iowa, where she began a long and fruitful collaboration with James Evans in the field of thin-film epitaxy. Maria remained at Iowa State until 1996, publishing an impressive series of highly cited papers on a number of topics including: submonolayer nucleation and growth of islands, multilayer kinetic roughening, and spatial organization during

Maria Bartelt, dressed in the light-blue hat and uniform worn by science students at the Universidade de Aveiro in Portugal, at her graduation parade in 1984.

nonequilibrium random sequential adsorption.

In 1996, Maria left Iowa State to become a physicist in the Computational Materials Science Department at Sandia National Laboratory in Livermore, where she continued her work on thin-film growth and expanded her research to include electromigration and stress voiding in interconnects, the creation of dislocation boundaries during metal deformation, and dislocation networks in complex plastic zones formed during indentation and fracture. Until her death, Maria remained an associate scientist for the Institute for Physical Research and Technology at Iowa State.

During the course of her remarkably productive career, Maria published more than 70 journal articles, book chapters, and proceedings; delivered many invited talks at national and international conferences; and organized numerous

symposia. She was a recognized leader in her field.

But for those of us who had the great fortune to work with Maria, the statistics on her accomplishments tell little about what she meant to us. Maria was a person of deep principles, profound determination, and unquenchable optimism; she never uttered a negative word. She cared genuinely about the welfare of her friends, colleagues, and group members, and her door was always open to offer a sympathetic ear or useful advice. Maria always had a smile to show the world, and by her positive example, she made those around her smile as well. She was a good person. We are better for having known Maria, and we will miss her.

Maria is survived by her husband, Tim; her twin sister, Maria de Fátima Taveira Pires de Carvalho; an older sister, Dalila Carvalho; her mother, Arcilia Gomes Taveira; and her beloved parrot, Spike.





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